

MODELS FOR THE MIGRATION OF ADDITIVES IN POLYOLEFINS

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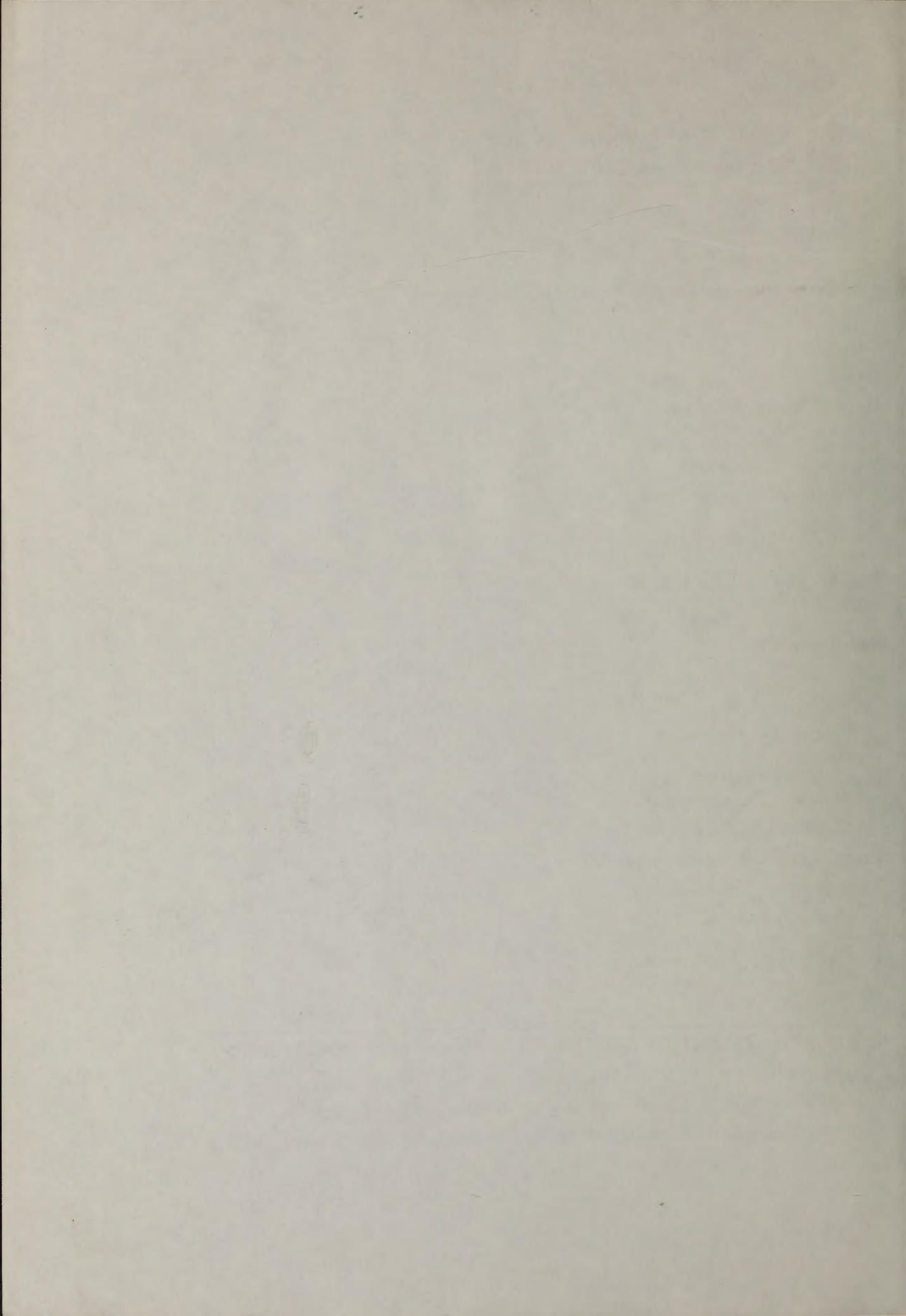


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Introduction

In addition to continuing our experimental and theoretical program as previously described, during the past quarter we have considered methods of organization and classification which could facilitate the understanding and use of our program outputs. We have also considered a number of specific technical questions that have been raised by FDA staff. Our program has focused initially on the class of polymers best described as polyolefins. These polymers represent the majority of plastics used in packaging applications and we feel that models of migration developed for the principal members of the class will be applicable to most members with only minor modifications. The technical requirement is that the polymers be equilibrium fluids rather than glasses. This requirement can be established by a glass transition temperature well below the use temperature or by evidence of some crystallinity at use temperatures. Using these criteria, a preliminary classification of polymers based on chemical structure can be developed as shown in Fig. 1.

We have found a formal decision tree to be a useful device to focus attention on the specific technical decisions involved in making regulatory judgments on indirect additive questions. A simple example of such a decision tree is given in Fig. 2 where it is presumed that choices of package sizes and suitable simulating solvents have already been made. The general form of this tree is, of course, independent of the polymer-migrant system involved but the functional forms used in the calculations of partition coefficients and diffusion constants are specific for the class of polymer involved. The determination of the appropriate functions for decisions is a principal objective of our work along with an assessment of the experimental data and methods needed as inputs.

Relation Between Partition Coefficient and Solubility

The second branch in the tree involves an estimation of K_o , the partition coefficient between the polymer and the food simulating solvent. In our Annual

Figure 1.

POLYOLEFINS

Essential characteristics for treatment as equilibrium fluid:

$T_g < -10^\circ\text{C}$; some crystallinity

<u>Chemical classification</u>	<u>(Examples)</u>
(1) linear alkane	(HDPE)
(2) branched alkane	(PP, PB, PH)
	branches straight chain aliphatic, ≤ 4 carbons
(3) copolymers of (1) with (2)	(LDPE)
(4) copolymers of (1) or (2) with $\leq 45\%$ vinyl acetate	(PE/PVAc)

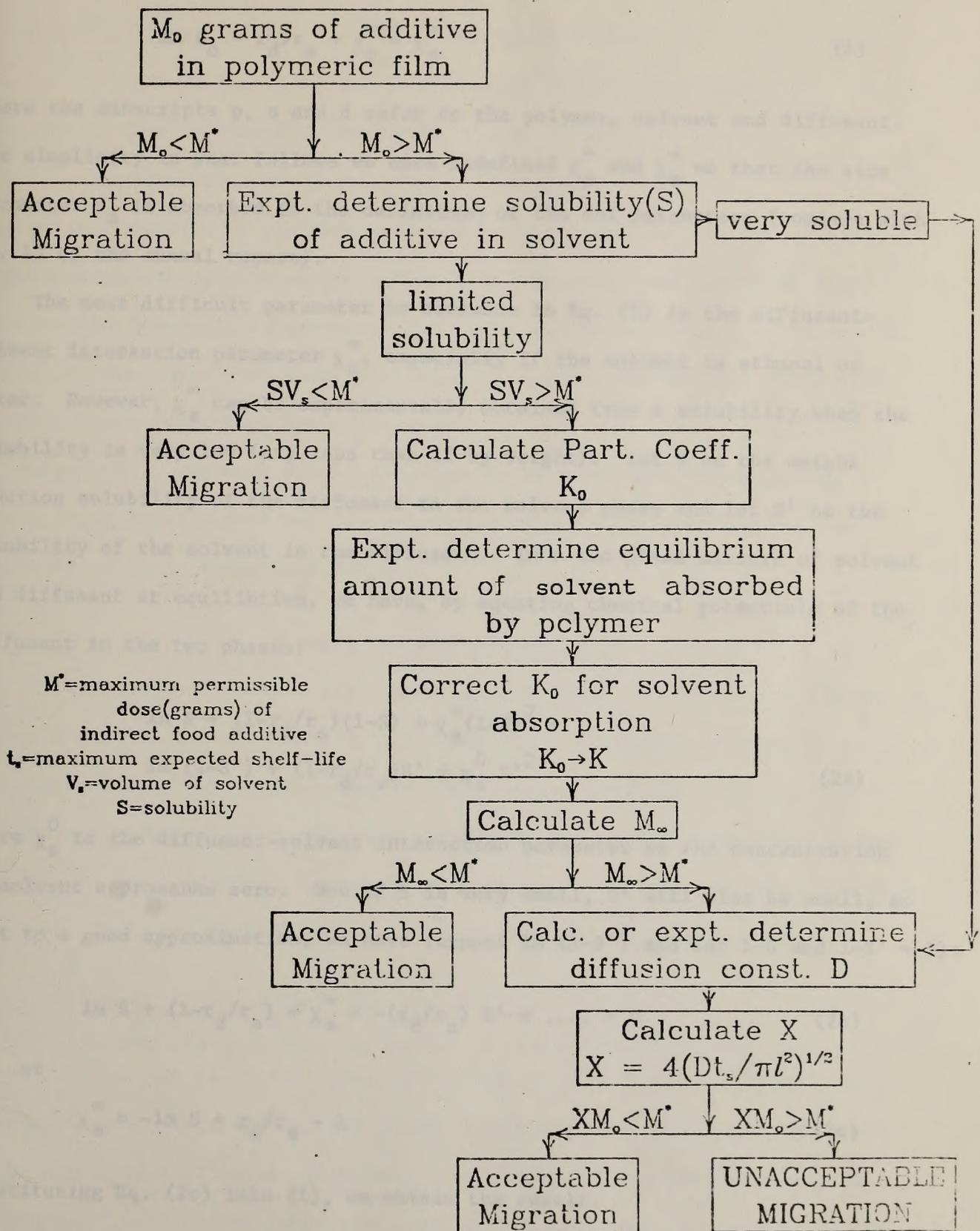
Polymers below will not generally have essential characteristics-----

(5) branched alkane		
(a) branches aliphatic > 4 carbons		polyheptane, etc.
(b) alicyclic		polyvinylcyclohexane
(c) branched		poly (4MP)
(d) aromatic		PS
(e) heteroatoms		PVC, Saran

Notes:

- (4) random PE/PVAc copolymers have crystallinity up to 45% VAc
- (5a) m.p. $\leq 70^\circ\text{C}$, (C_7) may be totally amorphous, class probably commercially unimportant
- (b) T_g of polyvinylcyclopentane = 75°
- (c) T_g between 20° and 40° for poly(4-methyl-1-pentene)
- (d) PS $T_g > 90^\circ$
- (e) PVC $T_g > 60^\circ$

Figure 2.



Report (NBSIR 79-1598) we derived an equation relating K_o to the infinite dilution interaction parameters χ_p^∞ and χ_s^∞ :

$$\ln K_o = r_d/r_s + \chi_p^\infty - \chi_s^\infty \quad (1)$$

where the subscripts p, s and d refer to the polymer, solvent and diffusant.

For simplicity in what follows we have redefined χ_p^∞ and χ_s^∞ so that the size parameter r_d is absorbed in the definition of the chi parameters (compare with Eq. 13 of the annual report).

The most difficult parameter to estimate in Eq. (1) is the diffusant-solvent interaction parameter χ_s^∞ , especially if the solvent is ethanol or water. However, χ_s^∞ can be experimentally obtained from a solubility when the solubility is very low (say less than 1% by weight). Let S be the weight fraction solubility of the diffusant in the solvent phase and let S' be the solubility of the solvent in the diffusant. In a two phase mixture of solvent and diffusant at equilibrium, we have, by equating chemical potentials of the diffusant in the two phases:

$$\begin{aligned} \ln S + (1-r_d/r_s)(1-S) + \chi_s^\infty(1-S)^2 &= \\ \ln (1-S') + (1-r_d/r_s)S' + \chi_s^0 S'^2 & \end{aligned} \quad (2a)$$

where χ_s^0 is the diffusant-solvent interaction parameter as the concentration of solvent approaches zero. Now if S is very small, S' will also be small, so that to a good approximation, we have (expand $\ln (1-S')$ and let $1-S$ and $1-S' = 1$):

$$\ln S + (1-r_d/r_s) + \chi_s^\infty \approx -(r_d/r_s) S' + \dots \approx 0 \quad (2b)$$

or

$$\chi_s^\infty \approx -\ln S + r_d/r_s - 1 \quad (2c)$$

Substituting Eq. (2c) into (1), we obtain the result:

$$\ln K_o = \ln S + \chi_p^\infty + 1 \quad (3)$$

Invariably, experimental values of χ_p^∞ are positive and usually fall in the range between zero and two.

However, larger values of χ_p^∞ might be expected when:

- (1) the diffusant/polymer combination is polar/non-polar
- (2) the diffusant is relatively large in size
- (3) the diffusant is relatively volatile.

Large χ_p^∞ are expected if the energetics are unfavorable, as in (1), or when χ_p^∞ has a large entropic component. The latter becomes more important the closer the diffusant is to its gas-liquid critical temperature T_c . Since, in general, T_c increases with molecular size, conditions (2) and (3) above tend to cancel one another to a certain degree.

Values of χ_p^∞ are most easily obtained by inverse phase chromatography.

We have begun experimental work in an evaluation of this technique and our progress to date is summarized below.

Inverse Gas Chromatography

The technique of inverse gas chromatography (IGC) can be used to obtain information about thermodynamic interactions and diffusional behavior of polymer/migrant pairs, as discussed in the previous quarterly report. The specific retention volume V_g is a key parameter in describing the equilibrium distribution of a volatile migrant or probe molecule between the vapor and polymer phase. This quantity is calculated from the following expression:

$$V_g = \frac{j \cdot F_c \cdot \Delta t \cdot 273}{T_c \cdot w_2} \quad (4)$$

where Δt is the net retention time, the period of time that a probe molecule is delayed in its flow through the column by dissolution in the polymer phase, F_c the corrected carrier gas flow rate, j a correction for pressure drop along the column, T_c the column temperature and w_2 the total mass of polymer in the

column. The partition coefficient is directly related to V_g by the expression:

$$K = V_g^0 \rho_2 T_c / 273 \quad (5)$$

where ρ_2 is the polymer phase density at T_c . Several considerations must be taken into account in the experimental determination of V_g . A sufficiently low concentration of the probe must be introduced to avoid saturating the limited amount of polymer, leading to an abnormally large vapor phase concentration of the probe and a corresponding anomalous value of the net retention time. If the surface to volume ratio of the supported polymer film is high, surface adsorption can make a significant contribution to Δt . When both bulk and surface sorption mechanisms occur the measured net retention volume, proportional to Δt , is given by the expression:

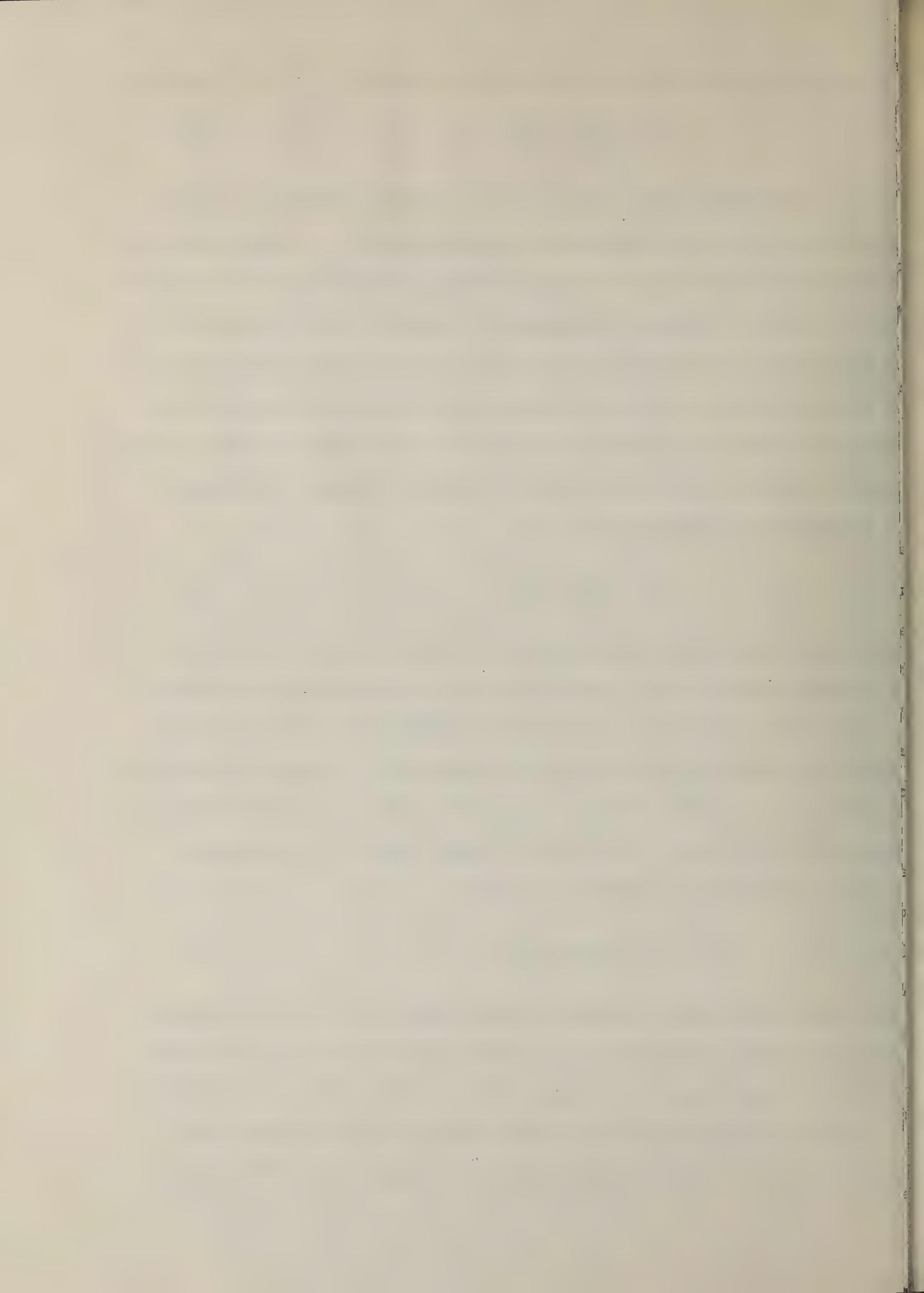
$$V_R = K_b w_2 + K_a a_2 \quad (6)$$

where K_b and K_a are the bulk and surface partition coefficients and a_2 the total polymer surface area. Carrier gas flow rate can also have an effect on V_g . If the flow rate is too rapid then partitioning of the probe molecules between the polymer and the vapor will be incomplete. A linear extrapolation of determinations at several flow rates to zero flow rate is usually necessary to eliminate this influence. The capillary column studies of Lichtenthaler et al (1) suggest a relationship of the form:

$$V_g = a \cdot \exp(-b F_c^2) \quad (7)$$

a and b being temperature dependent constants characteristic of each polymer-solvent pair. Such a relationship was found to give a good fit to their data at low flow rates, however, its derivation has limited physical justification.

Initial IGC experiments have employed NBS SRM 1475 high density poly-ethylene supported on glass beads packed into a copper column. The column

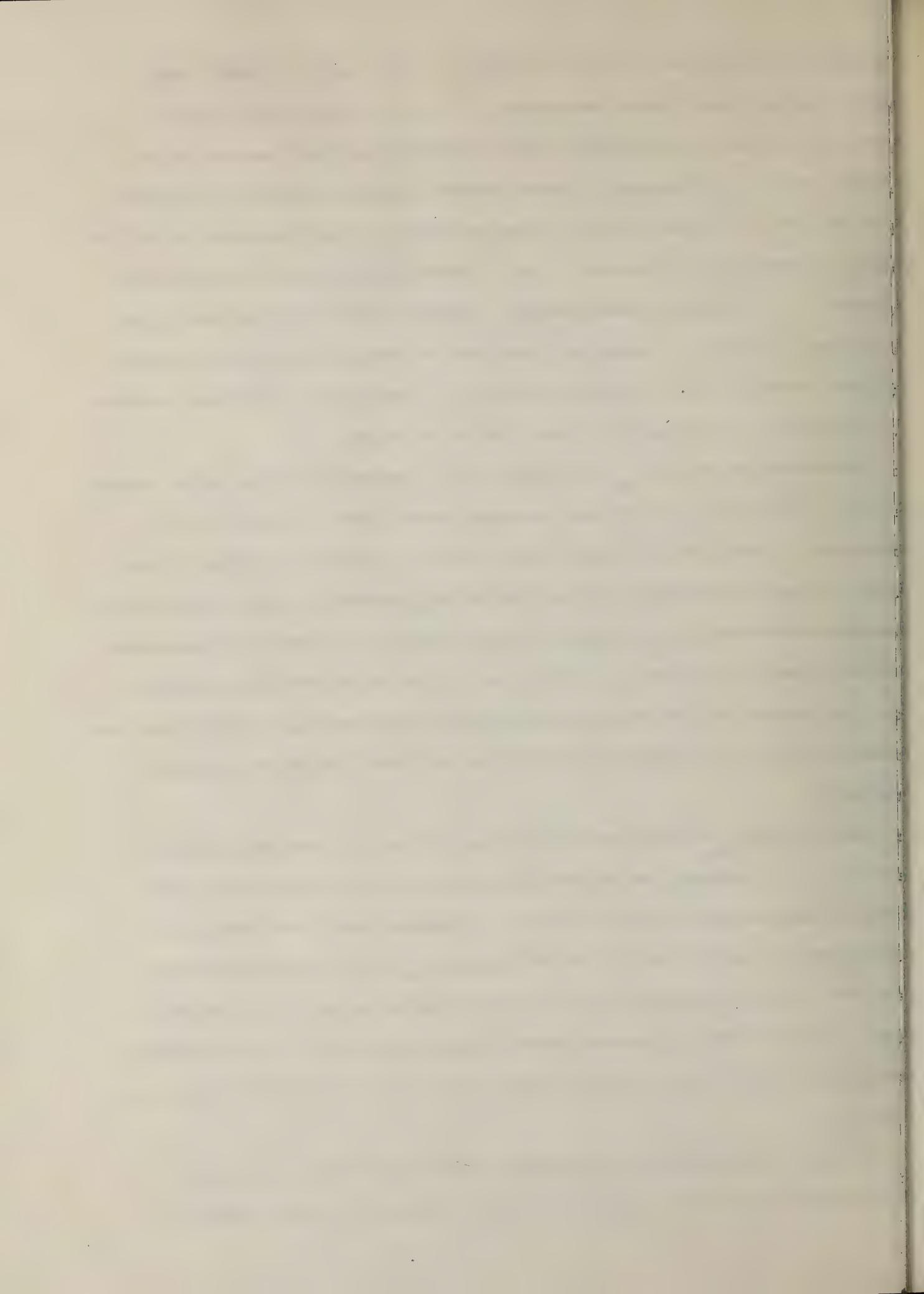


was prepared as described by Gray and Guillet (2) but with a slightly lower polymer loading than in their experiments. The net retention time between a methane marker and the decane probe was determined from the flame ionization detector output as a function of decane concentration and carrier gas flow rate at 70 and 150°C. The net retention time was found to remain constant at 70°C for decane concentrations below about 2 ppm. Concentrations below this amount were employed in all subsequent measurements. A linear relationship between V_g and F_c and one of the form of equation 7 were used to extrapolate to zero flow rate and gave retention volumes identical within 3%. The range of flow rates examined is insufficient to distinguish between the two relations.

Two determinations of V_g were made at 70°C, one before and one after heating to 150°C. Different V_g values were obtained in each case, 234 and 258 cm^3/g respectively. This 10% discrepancy could be due to a different percent crystallinity for each determination. Below the melting temperature, only the amorphous fraction contributes to bulk sorption and any change in the amount of amorphous material present will affect w_2 , and in turn V_g , as can be seen from equation (4). The accuracy of the percent crystallinity determination probably limits the maximum reliability to which V_g may be determined below the polymer melting temperature.

The limiting V_g at 150°C was found to be 70.2 cm^3/g . Previous studies by Braun et al. (3) employed two polyethylenes, Marlex 50 and Marlex 6050, and decane at temperatures from 145 to 153°C. Interpolation of their results to 150°C gives 74.6 and 75.1 cm^3/g for the limiting V_g of the two polyethylenes. These two values are identical within the experimental error of the procedure, about 1 to 2%, but differ from our measured value by about 6%. The discrepancy is thought to arise from instrumental limitations in our determinations as outlined below.

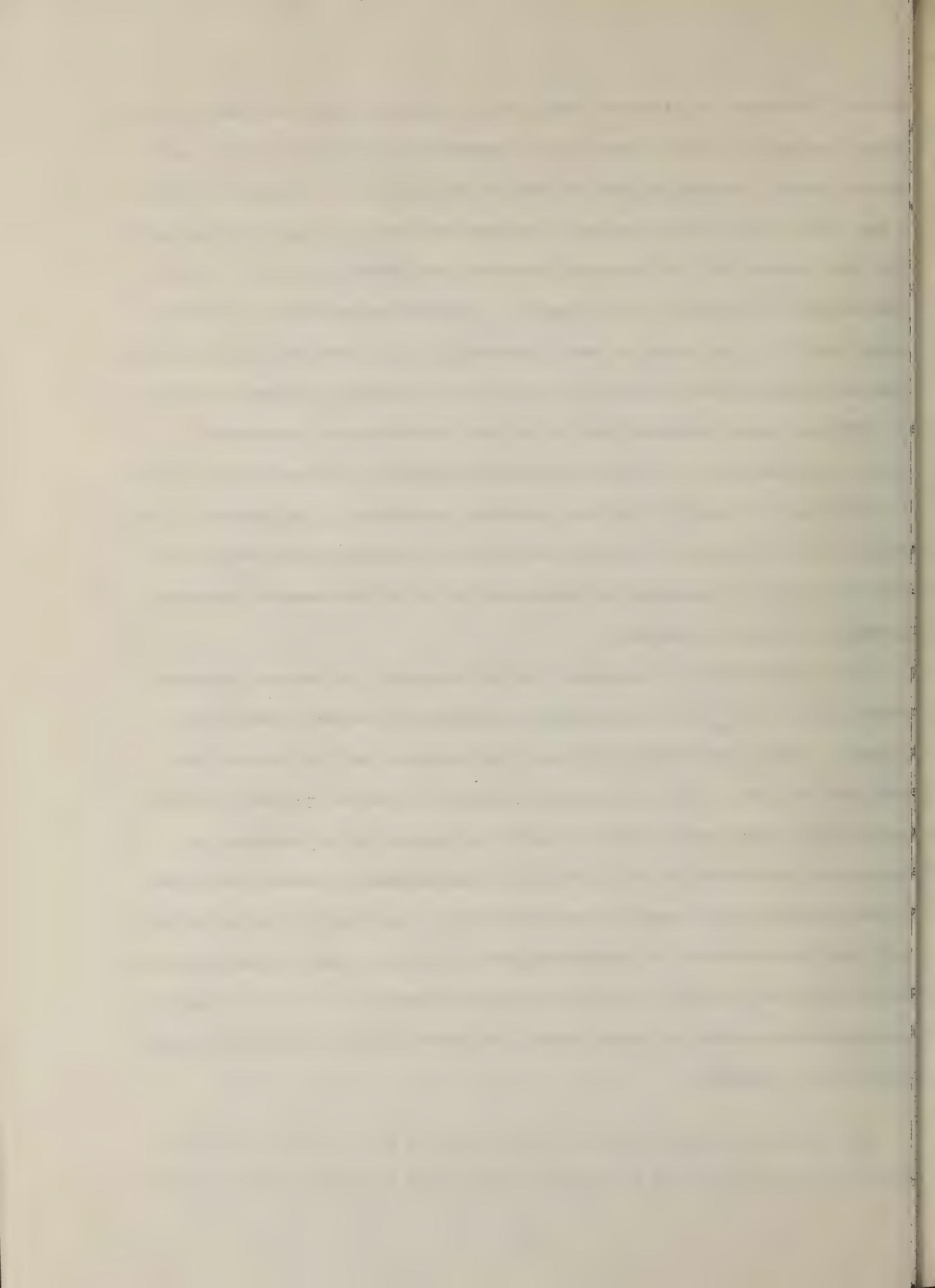
Several modifications of the apparatus will be undertaken to increase the accuracy of experiments performed in this laboratory. Column immersion



baths will be added to eliminate temperature variation along the length of the column, as great as 30°C in some cases, particularly near the injector and detector zones. Variability of the carrier gas flow rate, typically 5 to 7% at low flow rates, will be reduced by an improved pressure regulator and mass flow rate controller. An important parameter for determination of V_g is the total weight of polymer in the column, w_2 . As the concentration of polymer coated onto the glass beads is small, typically 0.5% by weight, precise determination of the polymer loading is critical for obtaining a reliable value of w_2 . The most common methods reported in the literature are gravimetric in nature. Calcination or solvent refluxing are employed to remove the film from the beads and the weight of polymer deposited is obtained by difference. The accuracy of these methods is being evaluated and instrumentation for precise weighing in inert atmospheres is available for use if the commonly employed procedures are found inadequate.

These improvements in apparatus and technique will allow more reliable determinations of V_g and the partition coefficient to be made from IGC experiments. The polymer-solvent interaction parameter and its entropic and enthalpic components will be obtained by study of selected systems at several temperatures. Such results will be useful in evaluating the validity of theoretical predictions of the equilibrium thermodynamic treatment described in the previous annual report. Better control of experimental variables will facilitate future studies of polymer-migrant diffusion. Gas chromatography will also be employed to detect the swelling-assisted release of various oligomers from polyethylene which may occur during the course of migration studies with radiolabeled compounds.

The third branch of the decision tree involves a calculation or an experimental determination of the amount of diffusion expected during the pro-



posed use life. One promising approach to calculation of diffusion constants uses a group contribution method to calculate the molar critical volumes of polymers and migrants. These values are combined with empirical relationships for calculating self-diffusion and mutual diffusion coefficients. All three of these calculations are currently under evaluation and the technical approach is summarized in the following.

Estimating Diffusion Coefficients in Polymer Liquids

Recently, Fedors⁴ has developed an empirical relation for calculating the self-diffusion coefficient of liquids. The equation is:

$$D_{11} = 4.5 \times 10^{-9} \frac{(V_c - V)T}{\eta V_c^{4/3}} \quad (8)$$

where D_{11} is the self-diffusion coefficient in units of cm^2/sec , η is the viscosity in poise and V_c and V are the molar volumes in cm^3/mole at the critical temperature and temperature T , respectively. He has shown that this equation works well for low as well as high molecular weight liquids. For non-associating organic liquids the average error is about 4%. Polymer liquids show a much larger but acceptable deviation. Self-diffusion coefficients for polymer liquids are notoriously difficult to measure because they are often very small. Experimental errors are often large. However, even with this difficulty in mind, calculated self-diffusion coefficients are within a factor of 2 or 3 of the experimentally observed values for several polymers including polyethylene.

Experimentally determined values of critical volumes V_c required in the above equation are often unavailable. Of course, this is always true of a polymer liquid. There are several methods of estimating V_c , but the simplest method is a group contribution method also due to Fedors⁵. In the Fedors' method:

$$V_c = 26.6 + \sum_i v_i \quad (9)$$

where the v_i are given below:

Table 1. Atomic and Structural Contributions to the Critical Volume

Atom	v_i cm ³ /mole	Structural Feature	v_i cm ³ /mole
C	34.426	3-membered ring	-15.824
H	9.172	4-membered ring	-17.247
O	20.291	5-membered ring	-39.126
O (alcohols)	18.000	6-membered ring	-39.508
N	48.855	Double bond	5.028
N (amines)	47.422	Triple bond	0.7973
F	22.242	Each additional ring attached directly to another ring (that is, biphenyl, naphthalene, etc.)	35.524

Critical volumes of polymers of known molecular weight can be estimated by the above method. A sample calculation to illustrate the method is given below for polyisobutylene.

To calculate the mutual diffusion constant, D_{12} , of component 1 in component 2 at infinite dilution we can use the Hildebrand relation^{6,7}:

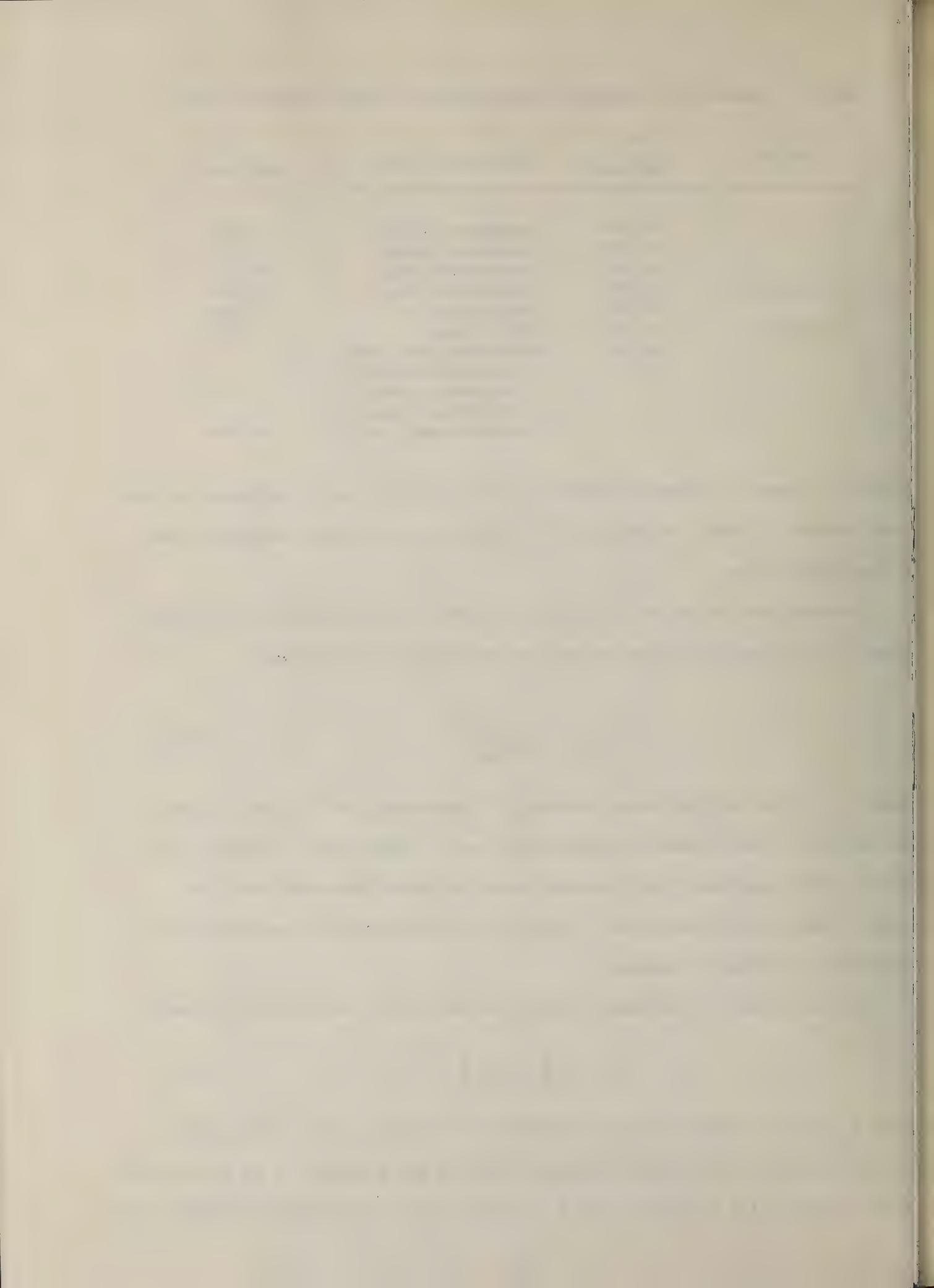
$$D_{12} = D_{11} \left(\frac{V_{c1}}{V_{c2}} \right)^{2/3} \quad (10)$$

where D_{11} is the self-diffusion constant of component 1 and V_{c1} and V_{c2} are the critical molar volumes of components 1 and 2, respectively. Sridhar and Potter⁷ have shown that the Hildebrand equation works relatively well in simple organic liquid mixtures. They did not investigate its applicability to diffusion in polymeric liquids.

For diffusion in a polymeric liquid, we write in a more familiar notation:

$$D_o = D_p \left(\frac{V_{cp}}{V_c} \right)^{2/3} \quad (11)$$

where D_o is the infinite-dilution diffusion coefficient of the diffusant in the polymer, V_{cp} is the critical molar volume of the polymer, V_c is the critical molar volume of the diffusant, and D_p is the polymer self-diffusion coefficient.



Sample Calculation of Self-Diffusion Coefficient for Polyisobutylene

$$M = 1.35 \times 10^6$$

$$\eta(35^\circ\text{C}) = 10.4 \text{ poise}$$

$$\rho(35^\circ\text{C}) = .914 \text{ g/cm}^3$$

$$\text{degree of polym} = 1.35 \times 10^6 / 56 = 2.4 \times 10^4$$

$$v_c = [26.6 + 4(34.43) + 8(9.172)] \times \text{DP}$$

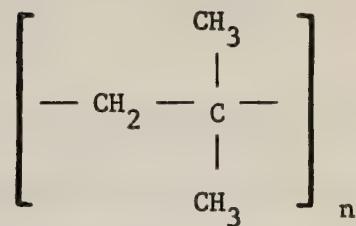
$$v_c = 237 \times 2.4 \times 10^4$$

$$v_c = 5.7 \times 10^6 \text{ cm}^3/\text{mole}$$

$$v = M/\rho = 1.35 \times 10^6 / .914 = 1.48 \times 10^6 \text{ cm}^3/\text{mole}$$

$$D_{11} = 4.5 \times 10^{-9} \frac{(1-v/v_c)T}{\eta v_c^{1/3}} = \frac{(4.5 \times 10^{-9}) (1 - 1.48/5.7) 308}{(10.4) (5.7 \times 10^6)^{1/3}}$$

$$D_{11} = 5.5 \times 10^{-10} \text{ cm}^2/\text{sec.}$$



We are currently testing Eq. (11) using the Fedors' equations (8) and (9) to calculate the D_p , V_{cp} , and V_c . Experimental polymer viscosity (zero shear) values which do not include the chain entanglement contribution are employed. The appropriate viscosity and density data are known for many common polymers including polyethylene.

Initial results are very encouraging. Equation (11) implies that the temperature dependence of diffusion in a polymer is dominated by the temperature dependence of the polymer viscosity. Experimentally, this is the qualitative behavior that is observed as emphasized in our first semi-annual report (NBSIR 78-1499).

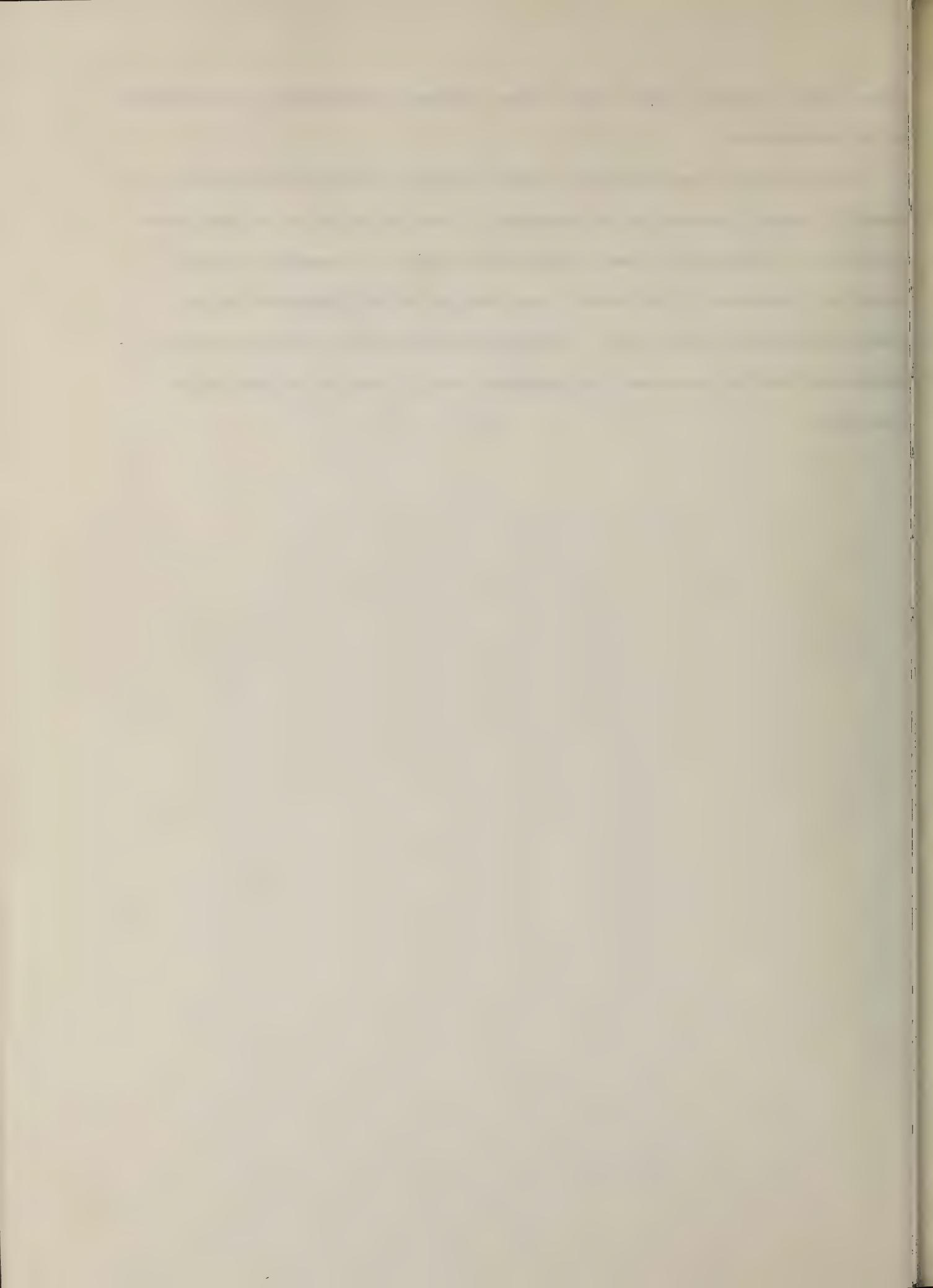
Review of Diffusion Constant Data

Diffusion constants for moderate molecular weight additives in common polymers are generally in the range of 10^{-6} to 10^{-12} cm^2/sec . depending on the temperature. In order to show this range more explicitly, we have compiled a brief review of appropriate literature data. The scope of this review has been limited to the compilation of diffusion constants (modeled by Fick's Law) as a function of temperature and activation energies (modeled by the Arrhenius equation) for migrants in polyolefins. The migrants selected are organic molecules or molecules with organic components. The emphasis is on higher molecular weight migrants, however, some low molecular weight substances are included for reference or when they compose part of a homologous series of additive materials covering a wide molecular weight range. Only data on two component systems (migrant and polymer) are included in the tables of this report.

In the following tables polyethylene has been subdivided into high density (linear) and low density (branched) materials. The large differences in diffusion constants for a single migrant in different polypropylene substrates

suggest that a similar subdivision between isotactic and atactic polypropylenes may be advantageous.

As mentioned in our Semiannual Report for 1978, diffusion in polymers is generally strongly concentration dependent, a fact which is not evident from the tables. Although the lowest concentration data were usually the ones chosen for inclusion in the tables, many studies in the literature do not provide much data on this point. In all cases, these data have received only preliminary critical appraisal and represent only a part of the available literature.



Key to Abbreviations of Methods

ΔP Sorption by pressure change measurements

GR Desorption by weight-loss gravimetry

GC Peak broadening in inverse phase gas chromatography

RA Radioactive tracer techniques

TL Permeation time lag measurement

IR Infrared microdensimetry



REF	MIGRANT	METHOD	DIFFUSION CONSTANT (cm ² /sec) $\times 10^8$												$\left(\frac{P}{\text{mol}}$							
			-30	-20	-10	0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160
4	Methane	ΔP																				
8	Ethane	GR	.068	.097	.286	.773	1.95	4.63														
7	Hexane	GR																				
7	3-Methyl Pentane	GR																				
7	Neohexane	GR																				
7	Cyclohexane	GR																				
7	Hexene-2	GR																				
7	Benzene	GR																				
10	"	GC																				
7	Octane	GR																				
7	Decane	GR																				
10	"	G.C.																				
6	Tetralin	G.C.																				

LOW DENSITY POLYETHYLENE (CONT.)

REF	MIGRANT	METHOD	DIFFUSION CONSTANT (cm ² /sec) $\times 10^8$												$\left(\frac{E}{kcal/mol}\right)$							
			-30	-20	-10	0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160
6	Cis-Decalin	G.C.																				9.0
6	Trans-Decalin	G.C.																				9.2
6	Dodecane	G.C.																				8.9
10	Tetradecane	G.C.																				8.9
1	Octadecane	RA																				12.2
7	P-Dioxane	GR																				18.0
7	Carbon Tetrachloride	GR																				19.8
6	3,5-Ditert Butyl-4-Hydroxy Toluene	G.C.																				10.0
6	3-Tert Butyl-4-Hydroxy Anisole	G.C.																				18.3
17	2,4-Dihydroxy Benzophenone	RA																				12.0
12	2-Hydroxy-4-Methoxy Benzophenone	RA																				16.4
12	2-Hydroxy-4-Butoxy	RA																				13.5
12	2-Hydroxy-4-Octoxy Benzophenone	RA																				13.5

LOW DENSITY POLYETHYLENE (CONT.)

REF	MIGRANT	METHOD	DIFFUSION CONSTANT (cm ² /sec) $\times 10^8$												(E) kcal mol							
			-30	-20	-10	0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160
16	2-Hydroxy-4-Octoxy Benzophenone	RA																				16.8
12	2-Hydroxy-4-Dodecoxy Benzophenone	RA																				14.0
12	2-Hydroxy-4-Octadecoxy Benzophenone	RA																				13.6
15	Didodecyl-3,3' Thio Bipropionate	RA																				12.4
15	N-Octadecyl-Diethan- olamine	RA																				12.3
15	1,1,3,Tris[2-Methyl-4- hydroxy-1-5-Tert Butyl] Phenol.	RA																				12.2
			.33	.54	.86	1.40	2.29	3.60														

HIGH DENSITY POLYETHYLENE

REF	MIGRANT	METHOD	DIFFUSION CONSTANT (cm ² /sec) x 10 ⁸												$\left(\frac{E}{kcal}\right)$ $\frac{mol}{mol}$									
			-30	-20	-10	0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180
4	Methane	AP																						12.6
13	Ethane	TL																						12.6
14	"	CR																						—
17	2- <i>q</i> -Hydroxy- Benzophenone	RA																						23.4
12	2-Hydroxy-4-Methoxy Benzophenone	RA																						17.4
12	2-Hydroxy- <i>t</i> -Butoxy Benzophenone	RA																						18.5
12	2-Hydroxy-4-Oktoxy Benzophenone	RA																						21.6
16	"	PA																						36.8
12	2-Hydroxy-4-Decadec- oxy Benzophenone	RA																						16.8
12	2-Hydroxy-4-Octa- decoxy Benzopheno- phene	RA																						17.0
18	Dodecanyl Dodecanante	I.R.																						1.5
18	Decosanyl Decocanate	I.R.																						—



POLYPROPYLENE

REF.	CHARACTER OF POLYMER	MIGRANT	METHOD	DIFFUSION CONSTANT (cm ² /sec) $\times 10^8$										(E) kcal/mol						
				0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	
5	75% Cryst.	n-Heptane	RA	.0028	.0091	.027	.071	.200	.50	---	---	---	---	---	---	---	---	---	---	
5	75% Cryst.	Toluene	RA	.010	.047	.105	.23	.50	1.00	---	---	---	---	---	---	---	---	---	---	
2	Isotactic	"	GR	37.	37.	37.	37.	37.	37.	37.	37.	37.	37.	37.	37.	37.	37.	37.	37.	
19	2	Isotactic p-Xylene at 100°	GR	126	126	126	126	126	126	126	126	126	126	126	126	126	126	126	126	
5	75% Cryst.	Methyl Cyclohexane	RA	.0013	.0042	.013	.034	.092	.24	---	---	---	---	---	---	---	---	---	---	
2	Isotactic	"	GR	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	
2	Isotactic p-Xylene at 100°	"	GR	59	59	59	59	59	59	59	59	59	59	59	59	59	59	59	59	
2	Isotactic	Isooctane	GR	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	
2	Isotactic p-Xylene at 100°	"	GR	59	59	59	59	59	59	59	59	59	59	59	59	59	59	59	59	
17	Isotactic	2,4-Dihydroxy Benzophenone	RA	.0049	.0230	.155	.155	.155	.155	34.0	34.0	34.0	34.0	34.0	34.0	34.0	34.0	34.0	34.0	34.0
11	Isotactic 63% Cryst.	2-Hydroxy,4-Methoxy- benzophenone	RA	.36	.75	1.46	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78



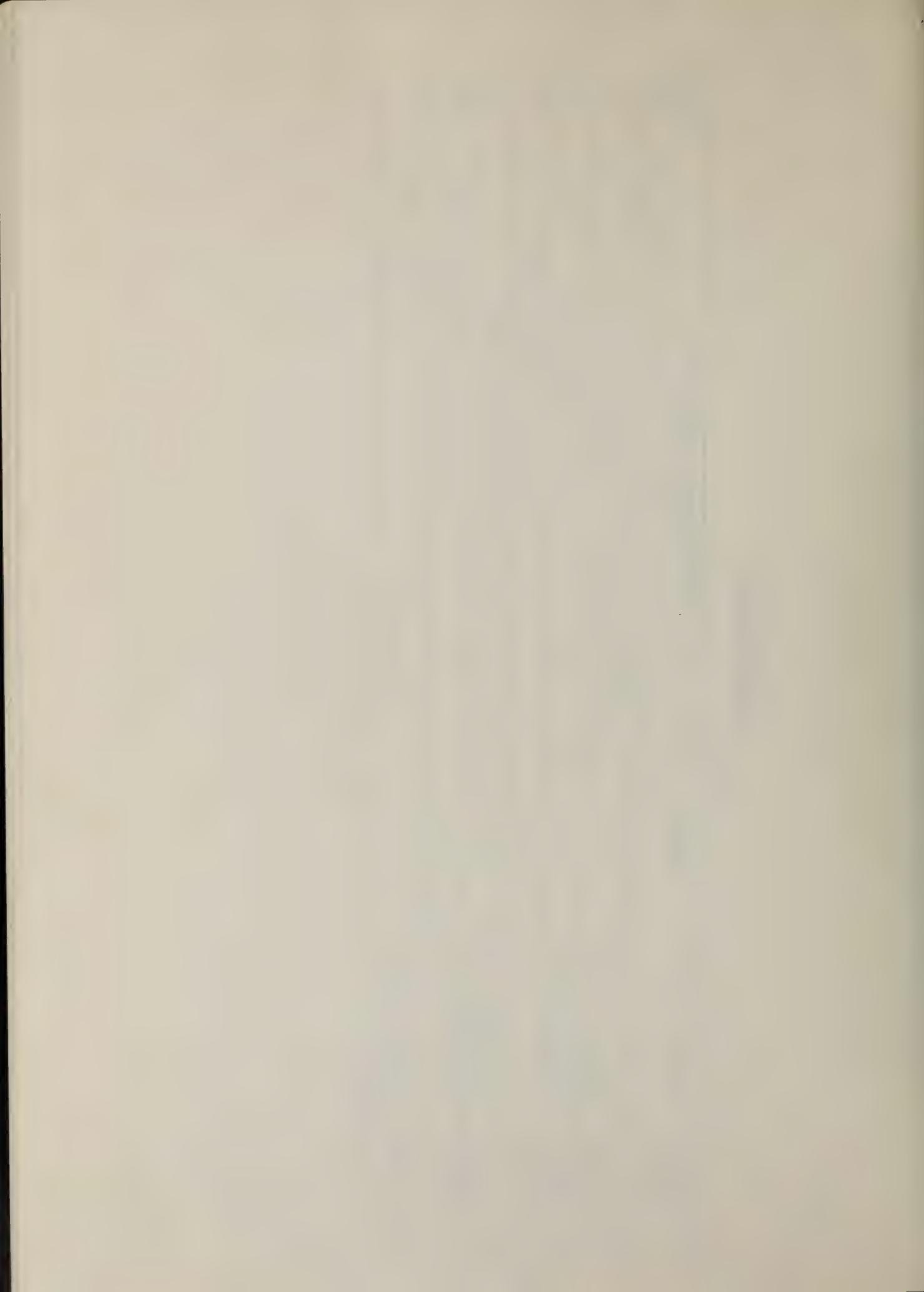
POLYPROPYLENE (CONT.)

REF	CHARACTER OF POLYMER	MIGRANT	METHOD	DIFFUSION CONSTANT (cm ² /sec) x 10 ⁸												$\left(\frac{E}{kcal}\right)$ (mol)	
				0	10	20	30	40	50	60	70	80	90	100	110	120	
12	Stereoblock	2-Hydroxy, 4-Methoxy- benzophenone	RA														12.1
11	Isotactic	2-Hydroxy, 4-Butoxy- benzophenone	RA														19.5
12	Stereoblock	"	RA														14.9
16	Isotactic	2-Hydroxy, 4-Octoxy- benzophenone	RA														23.6
11	Isotactic	"	RA														23.6
12	Stereoblock	"	RA														16.7
11	Isotactic	2-Hydroxy, 4-Dodecoxy- benzophenone	RA														21.3
12	Stereoblock	"	RA														20.0
11	Isotactic	2-Hydroxy, 4-Octadecoxy Benzophenone	RA														23.7
12	Stereoblock	"	RA														18.2
11	Isotactic	2-Hydroxy, 4-Octadecoxy Benzophenone	RA														17.1
12	Stereoblock	"	RA														19.1
11	Isotactic	Dimethyl 3,3' Thio Di- Propionate	RA														18.6
11	Isotactic	Dihexyl 3,3' Thiodipropyl- onate	RA														18.6



POLYPROPYLENE (CONT.)

REF	CHARACTER OF POLYMER	MIGRANT	METHOD	DIFFUSION CONSTANT (cm ² /sec) x 10 ⁸										$\left(\frac{E}{\text{kcal}}\right)$ mol						
				0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	
12	Stereoblock 63% Cryst.	Dihexyl 3,3' Thiodipropionate	RA	.087	.259	.715														19.2
11	Isotactic 63% Cryst.	Didodecyl 3,3' Thiodipropionate	RA																	20.3
15	60% Cryst.	"	RA																	19.8
11	Isotactic 63% Cryst.	Dihexadecyl 3,3' Thiodipropionate	RA																	21.5
15	60% Cryst.	N-Octadecyl-Diethanolamine	RA																	20.5
15	60% Cryst.	1,1,3-Tri [2-Methyl-4-Hydroxy-5-Tert Butyl] Phenol	RA																	20.5
																				22.3
																				22.3



POLY (ISOBUTYLENE)

REF	MIGRANT	METHOD	DIFFUSION CONSTANT (cm ² /sec) $\times 10^8$												$\left(\frac{E}{kcal}\right)$ mol							
			0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180	190
1	n-Octadecane	RA														19.7	24.6					9.9
1	n-Octadecanol	RA														15.6	31.7					10.0
1	Stearic Acid	RA														7.4	12.2					7.0
1	n-Octadecyl Stearate	RA														4.6	9.3					10.2

HYDROGENATED POLYBUTADIENE (5% UNSATURATED)

REF	MIGRANT	METHOD	DIFFUSION CONSTANT (cm ² /sec) $\times 10^8$												$\left(\frac{E}{kcal}\right)$ mol							
			0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180	190
1	n-Octadecane	RA														8.0	14.0	23.1				10.8

POLY (4-METHYL PENTENE-1)

REF	MIGRANT	METHOD	DIFFUSION CONSTANT (cm ² /sec) $\times 10^8$												$\left(\frac{E}{kcal}\right)$ mol								
			0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180	190	200
15	Didodecyl,3',3',Thio- Propionate	RA														3.15	4.30	5.81	7.85	10.7	14.6	14.5	
15	1,1',3-Tris[2-Methyl-4- Hydroxy-1-5-Tert Butyl] Pheno1	RA														.260	.371	.527	.759	1.07	1.52	2.20	14.2



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As mentioned in previous reports, the diffusion constant for a migrant should correlate with molecular size and flexibility rather than strictly with molecular weight. With this in mind, the general effects of branching or the incorporation of ring structures can be predicted in that these structures are somewhat bulkier relative to the linear structure of the same molecular weight. Quantitatively, however, these differences are expected to be rather minor (less than a factor of 2) except for extreme cases. An example of these effects is given in the first table of the diffusion data where the diffusion of various C₆ structural isomers is compared in low density polyethylene. Increased branching in 3-methyl pentane and neo-hexane lowers the diffusion coefficient relative to n-hexane as does the incorporation of a ring structure in the case of cyclohexane.

The experimental determination of diffusion constants generally involves the analysis of data according to a presumed model. We have previously discussed ideal diffusion models but the possibility of temperature extrapolation and the scaling of sample thicknesses are of particular interest so we will discuss these aspects in more detail.

Errors in Temperature Extrapolations

Let the diffusion coefficient of a migrant in a polymer be D₁ at a temperature T₁ with an activation energy E. Then the diffusion coefficient at a temperature T₂ may be extrapolated to be:

$$D_2 = D_1 \exp [E/R(1/T_1 - 1/T_2)] \quad (12)$$

Let an estimated activation energy E + ΔE in error by ΔE be used instead of the true activation energy E. Then the error in the predicted diffusion coefficient D₂' at temperature T₂, expressed in percent, is:

$$100 \frac{D_2' - D_2}{D_2} = 100 \exp \left[\frac{\Delta E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right] - 100$$

where R is the gas constant and the temperature T_1 and T_2 are in degrees Kelvin. Notice that the extrapolation error, when expressed in percent, depends only on the error in the activation energy and on the temperatures; the percent error does not depend on the activation energy or the diffusion coefficient.

Table 2 gives percent errors of the extrapolated diffusion coefficient for extrapolations from 80°C to 60 , 40 and 20°C for errors ΔE in the estimated activation energy of 2 , 5 , 10 and 15 kcal/mole.

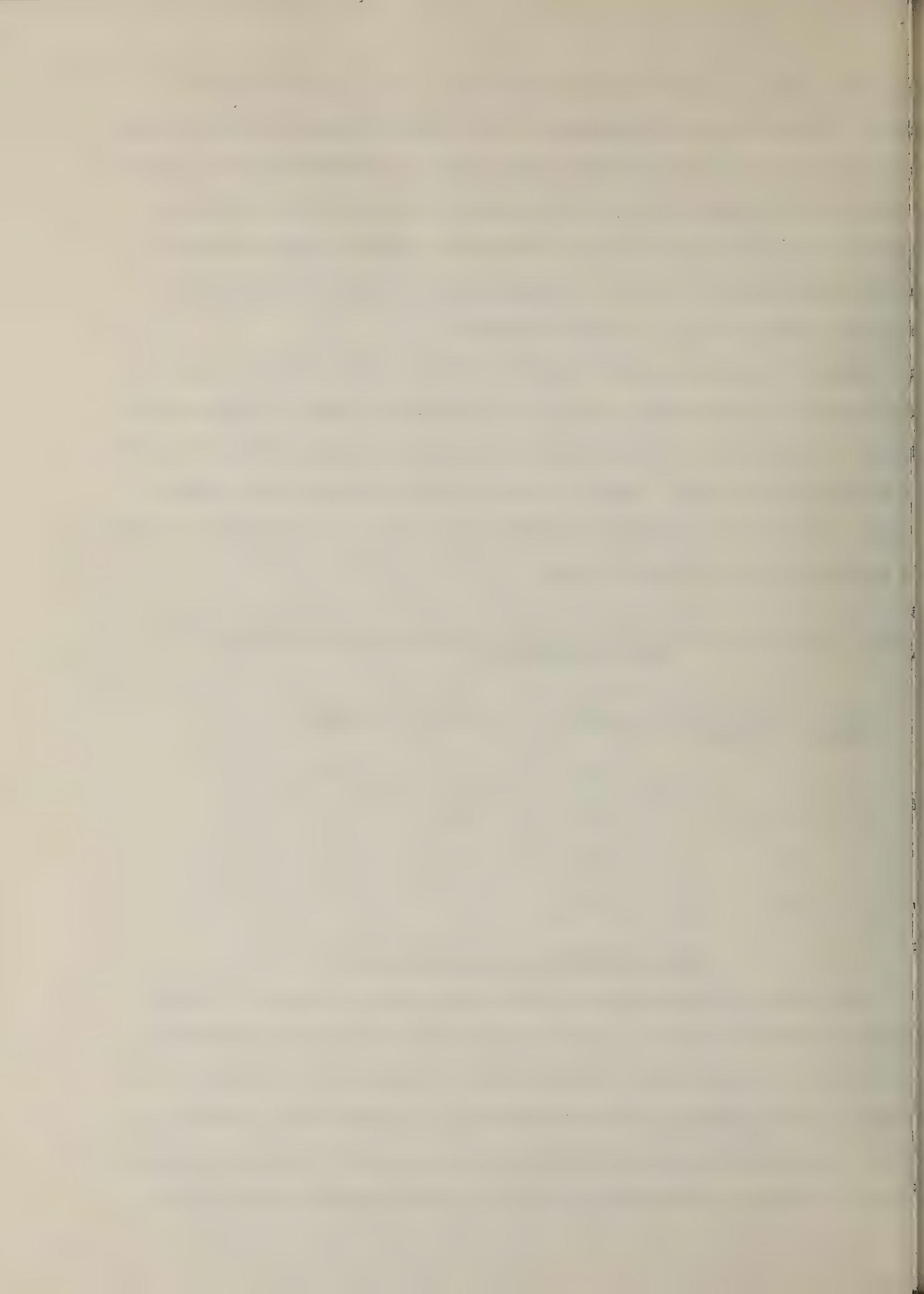
Table 2 shows that accurate values of the activation energy are required for temperature extrapolation. Thus, if the activation energy is estimated to within 2 kcal/mole, the diffusion coefficient may be extrapolated for 80 to 20°C with less than 50% error. However, if the activation energy is only known to within 10 kcal/mole, the diffusion coefficient may not be extrapolated from 80°C to even 60°C with less than 50% error.

Table 2. Percent error in diffusion coefficients extrapolated from 80°C to given temperature.

Error in activation energy, kcal/mole	20°C	40°C	60°C
2	44	31	16
5	77	60	35
10	95	84	58
15	98	93	72

Effect of Thickness on Migration Rate

The theoretical migration curve for a film is shown versus Dt/l^2 in fig. 3 and versus $\sqrt{Dt/l^2}$ in fig. 4. A is the area of the film, l is the thickness of the film and C is the initial concentration of the additive in the film, so the ordinate is the fraction of the additive that has migrated out of the film in time t . The migration is seen to depend on the ratio t/l^2 . Thus the migration curves of different thicknesses of film (with other parameters the same) are



plotted versus t/ℓ^2 , they should superimpose. This is observed for experimental migration curves in the next section. Simpler scaling laws apply if the migration is very slow or very fast compared to the times of service.

The case of slow migration is illustrated in figure 5. The migration per unit area is shown versus the square root of the time for three film thicknesses. The migration is seen to be independent of the film thickness, in fact, to be proportional to the square root of the time, for sufficiently small times. Equivalently, the sheet may be considered infinitely thick for sufficiently small times. The condition for the migration to be independent of film thickness is:

$$\ell > 3.76 \sqrt{Dt} \quad (13)$$

Thus, if equation 13 is satisfied for the service and test time of the film, migration measured at one film thickness may be used for another film thickness. In this case, the migration per unit area is given by:

$$\frac{M_t}{A} = \frac{4 \sqrt{Dt}}{\sqrt{\pi}} C \quad (14)$$

For very fast migration, the amount of migration is the total amount of additive in the film, so:

$$\frac{M_t}{A} = \ell C \quad (15)$$

so the migration per unit area is proportional to the thickness of the film.

Eq. 15 will apply within one percent for times

$$t > 0.11 \ell^2/D \quad (16)$$

The above results apply for ideal, Fickian diffusion. They probably also apply approximately for extraction when the rate of diffusion also depends on the rate of diffusion of the solvent into the plastic film. This will be investigated in the next quarter.

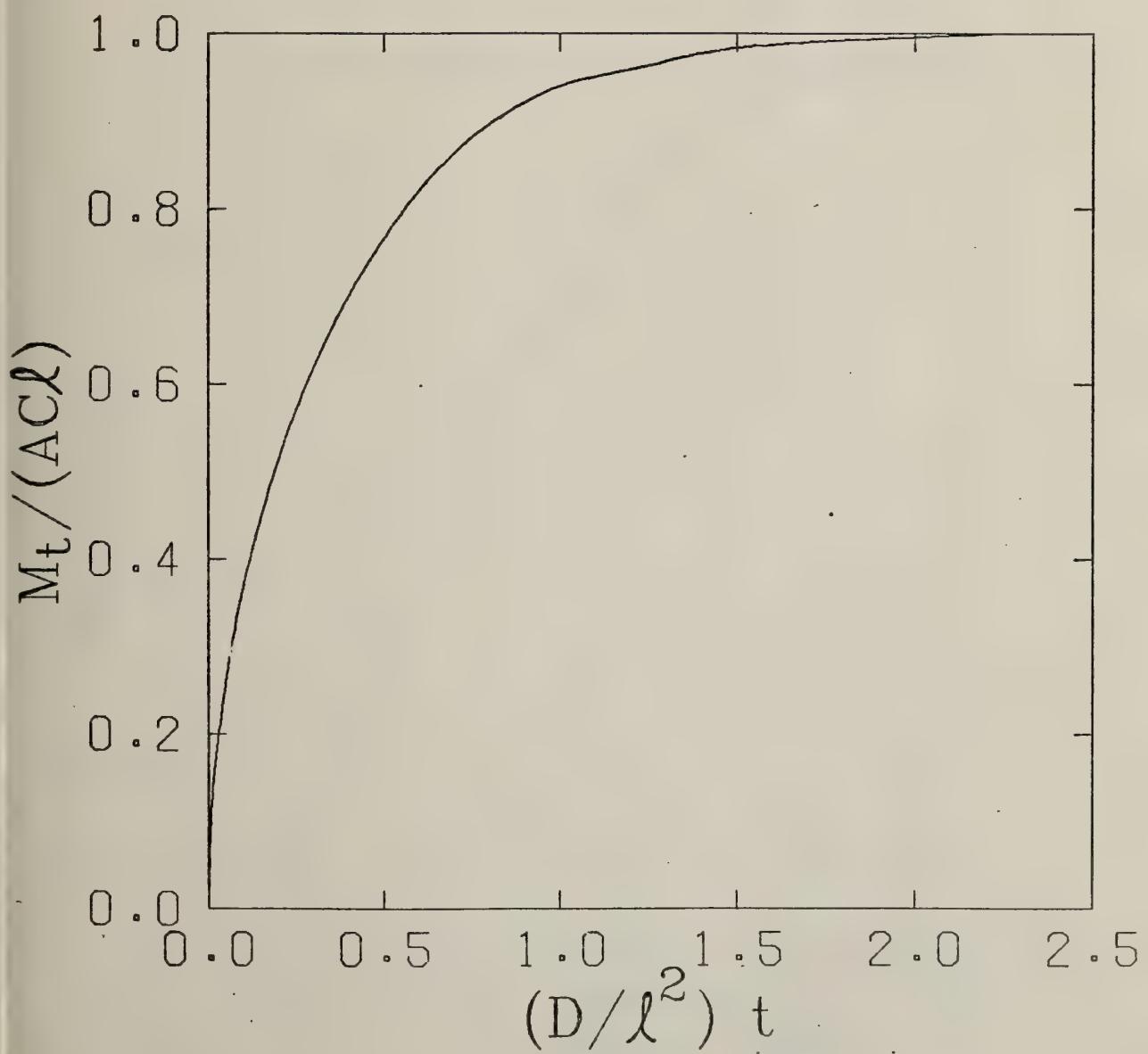


Figure 3. Migration Curve of a film versus Dt/ℓ^2 .



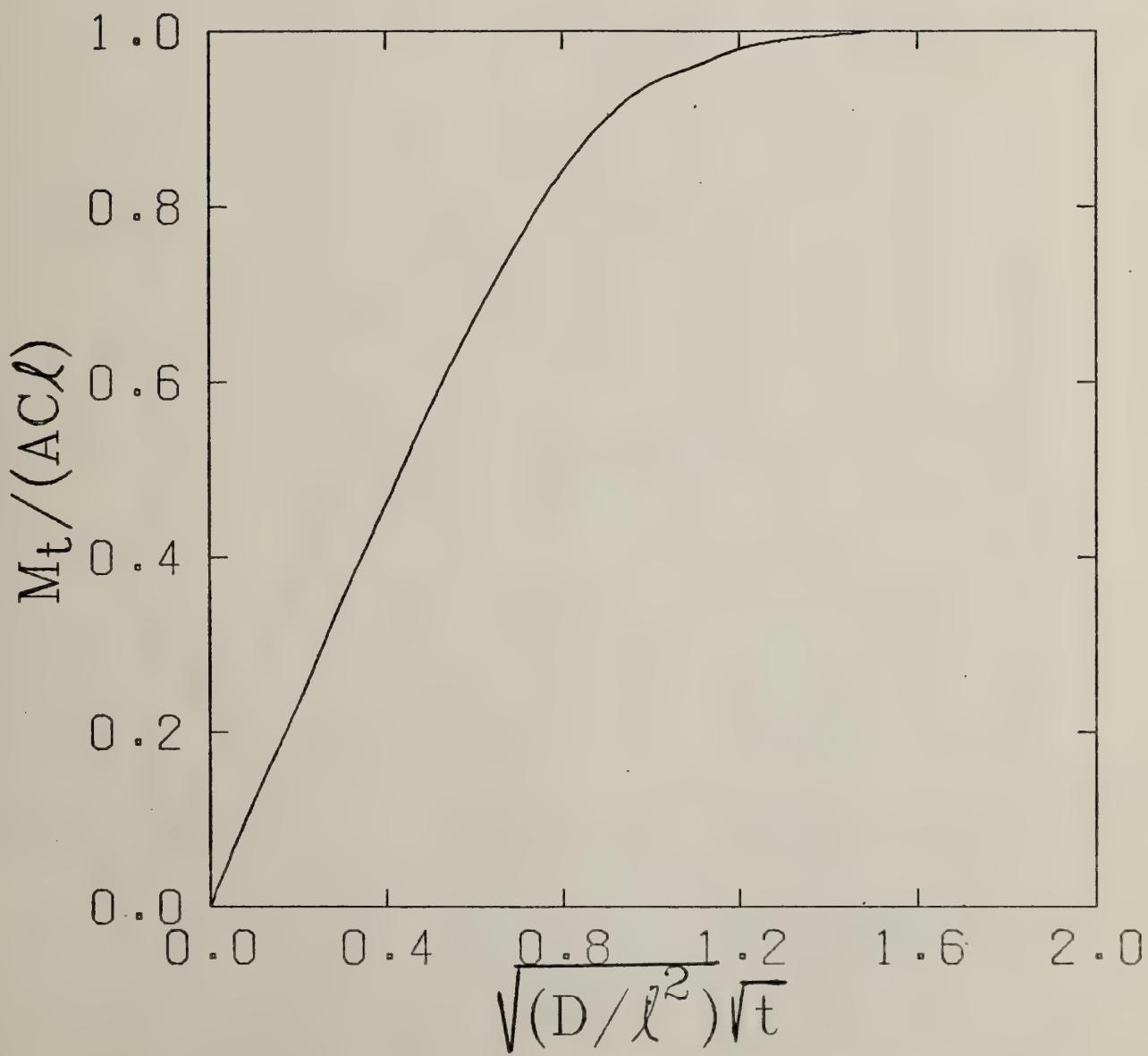


Fig. 4. Migration curve of a film versus square root of Dt/λ^2 .

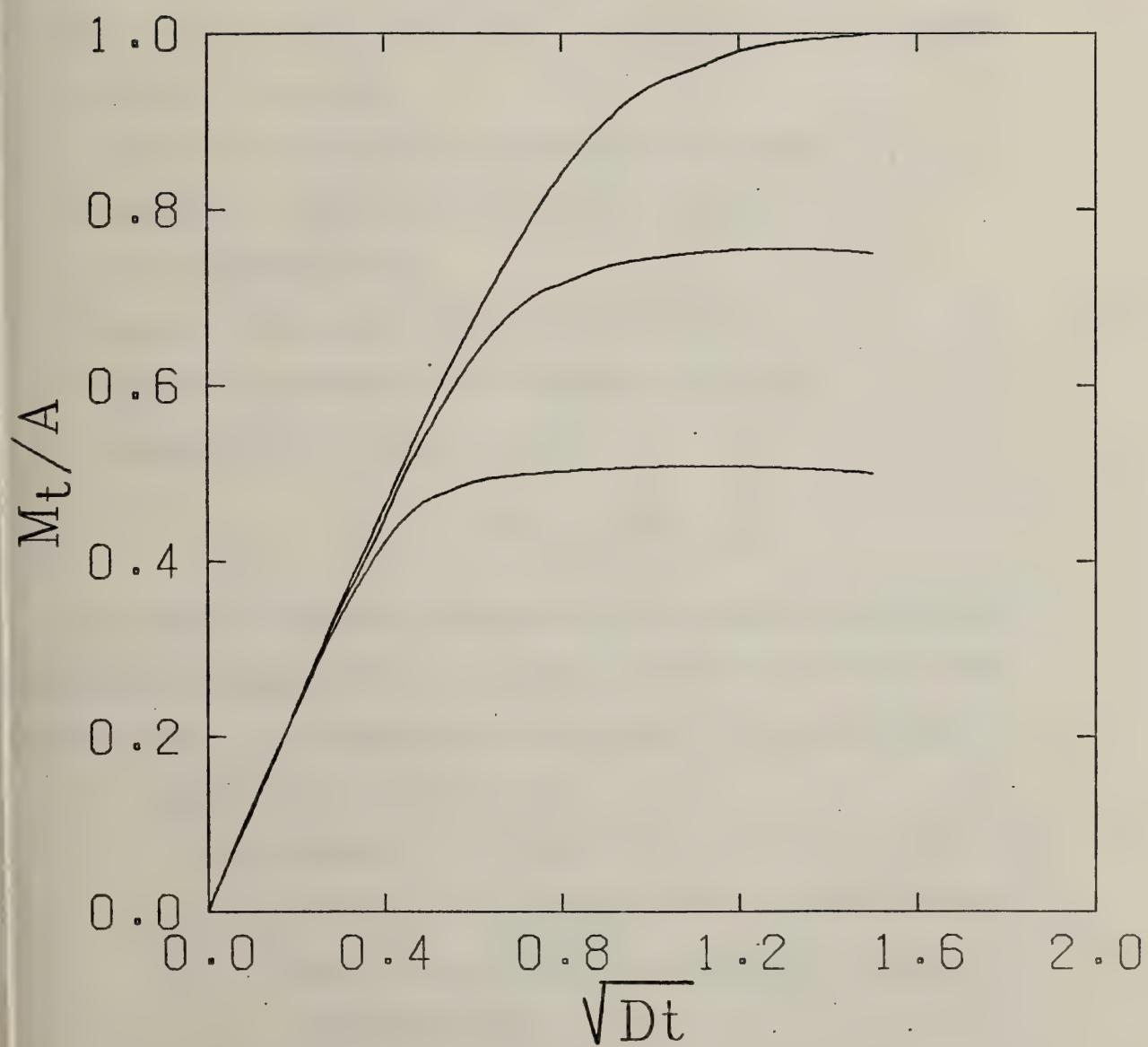


Fig. 5. Migration curves of films of three thicknesses.



Experimental results that pertain to thickness scaling are given in the following section dealing with our laboratory measurements of oligomer migration.

Laboratory Measurements of Oligomer Migration

In the experimental migration work we are looking for the correlations of migration of adjuvants from polymers into solvents, along with other factors such as additive concentration, polymer crystallinity, specimen thickness, etc. In the case of limited solubilities, the equilibrium partition coefficient may also be determined.

After the new coding scheme, the following topics are presented:

- methods of extraction
- possibility of eliminating thickness as a variable
- migration of $C_{18}H_{38}$ into ethanol/water mixture
- partition coefficients
- search for simulating solvent for food oil
- migration of oligomers from branched polyethylene
- planned work for the next quarter

Coding Scheme

In order to convey more information in the sample coding system, the following coding scheme is now used in place of the coding scheme used previously. The sequential coding scheme is described below:

(1) 1st character -- solvent type

C = Corn oil

E = Ethanol, with fractional ethanol content following the letter E to denote the composition of aqueous ethanol mixtures

H = Heptane

O = Octadecane

T = Trioctanoin

(2) 2nd character -- sample plaque designation (LPE - linear polyethylene,
BPE - branched polyethylene)

ℓ mm	$C_{18}H_{38}\%$	0.01	1	5
0.2 LPE		D	B	F
0.7 LPE		C	A	E
0.7 BPE			G	

Sample E and F were saturated with $C_{18}H_{38}$.

(3) Extraction temperature in $^{\circ}C$ follows sample plaque designation
(4) Limited volume extraction experiments are followed by a letter
L, otherwise the experiments are carried out as to simulate
infinite solvent volume
(5) Additional experiments with similar conditions are distinguished
by a dash followed with sequential numbers

We are in the stage of finishing all the planned experimental observations
on the migration of $C_{18}H_{38}$ from linear polyethylene into various solvents.
Only 8 of the 42 experiments are in their last stages at the present time, the
rest of the experiments have already reached completion. Selected results are
presented in the following section. Complete discussion and correlation of all
42 experiments will probably appear in the next report. The experimental con-
ditions for all 42 experiments are summarized in the following tables:

I. $C_{18}H_{38}$ into Heptane

t $^{\circ}C$	$C_{18}H_{38}\%$	0.01	1	5
24		HC24 HD24	HA24L HA24 HB24	
30		HC30	HA30	HE30
60		HC60	HA60-1 HA60-2	

II. $*\text{C}_{18}\text{H}_{38}$ into $\text{C}_{18}\text{H}_{38}$

$t^{\circ}\text{C}$	$*\text{C}_{18}\text{H}_{38}\%$	0.01	1	5
30		OC30	OA30	OE30
60		OC60	OB60	OE60 OF60

III. $\text{C}_{18}\text{H}_{38}$ into Ethanol/water system

Ethanol, %	$\frac{\text{C}_{18}\text{H}_{38}\%}{^{\circ}\text{C}}$	0.01	24	1	30	60
0		E.0C60L		E.0B24L		
10		E.1C60L				
30		E.3C60L				
50		E.5C60L				E.5A60L E.5B60L E.5B60
70						E.7A60L
90						E.9A60L E.9B60
100		EC60L	EB24L EB24	EB30L	EB60	

IV. $\text{C}_{18}\text{H}_{30}$ into Corn Oil

$t^{\circ}\text{C}$	$\text{C}_{18}\text{H}_{38}\%$	0.01	1
30		CC30L	CA30L
60		CC60L	CA60L

V. $\text{C}_{18}\text{H}_{30}$ into Trioctanoin

$t^{\circ}\text{C}$	$\text{C}_{18}\text{H}_{38}\%$	0.01	1
30		TC30L	TA30L
60		TC60L	TA60L

In Tables I to V, where there is more than one experimental code in one of the temperature-concentration combinations, they are included to show one of the following three effects:

- (a) reproducibility: HA60-1, HA60-2
- (b) thickness variations: HA24L, HA24, HB24
HC24, HD24
OE60, OF60
E.9A60L, E.9B60
E.5A60L, E.5B60L

or (c) the differences between limited volume extraction and infinite volume extraction detailed in another section.

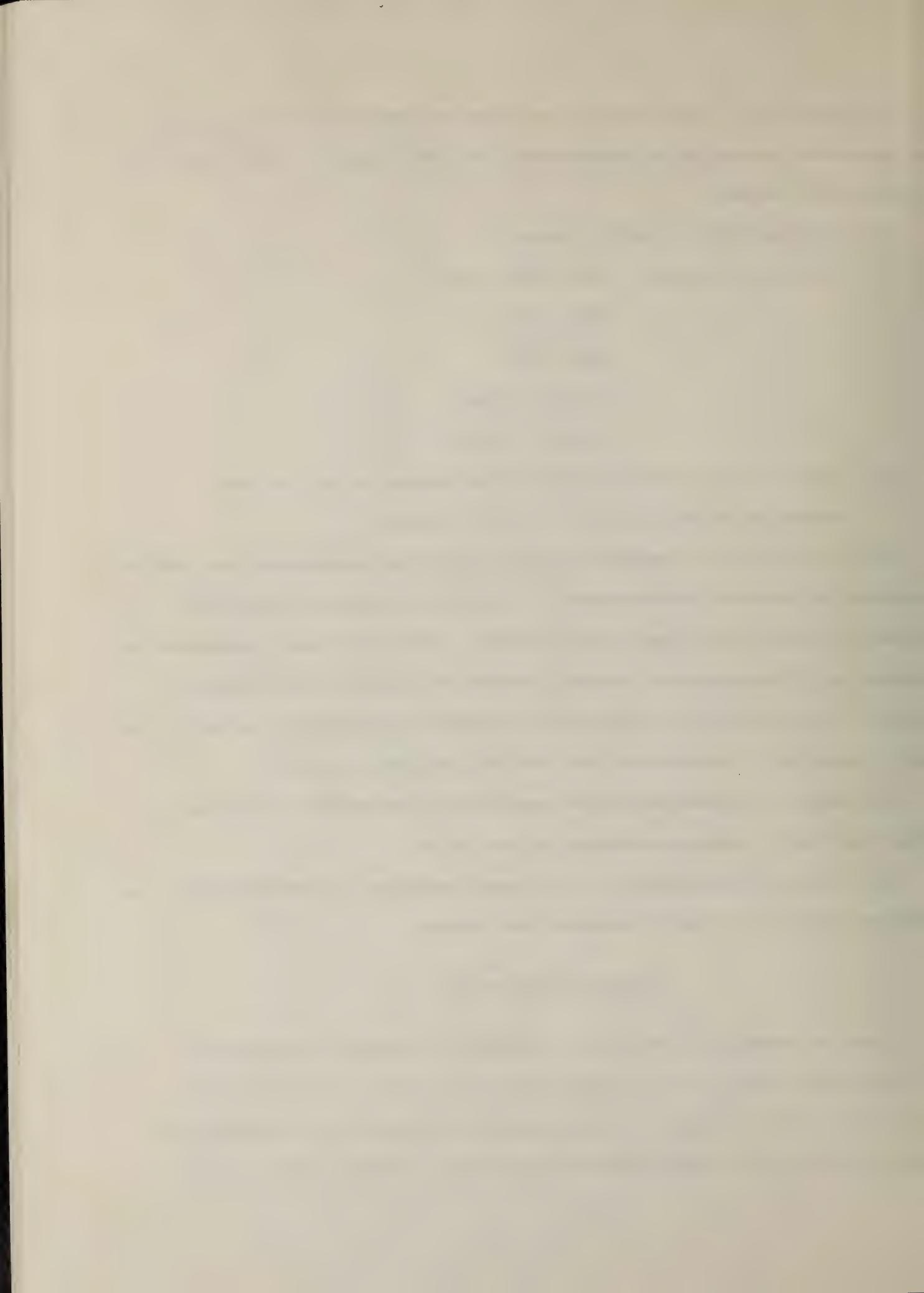
For each table, the experiments listed for the same temperatures are used to determine the concentration dependence of the migration behavior, which may include the plasticizing effect of the additive. There are clearly concentration dependencies of the migration behavior; however, the effect is difficult to separate from the effect of swelling of the polymer by the solvent, except in the case of migration of the additive into the bulk additive as solvent.

The temperature dependence may be seen by the experiments listed in each column denoting the same concentration in each table.

By collecting the experiments at the same temperature and concentration from different tables, the effect of solvents may be seen.

Methods of Extraction

There are essentially two different methods of extraction mentioned in the FY78 Annual Report, viz., (1) simulated infinite volume extraction, and (2) limited volume extraction. A third method was suggested as a variation of method (2), but has not been applied because of more demanding sample require-



ments. For solvents with high solubility or miscibility with the additive, methods (1) and (2) will give identical extraction results. However, for solvents with limited solubility, method (1) may yield erratic results depending on whether an equilibrium partition is approached or not before the replenishment of the solvent. Therefore method (2) is preferred, in general for both high and low solubility solvents. Only in the case of known high solubility should method (1) be used to simplify experimental procedures. Such agreement may be seen by comparing the results of pairs of experiments such as (HA24L, HA24) and (EB24L, EB24) shown in last annual report.

At 60°C the solubility of $C_{18}H_{38}$ in 90% ethanol is about 3%. Still, fairly good agreement between the pair of experiments E.9A60L and E.9B60 is obtained by reducing the thickness of the samples by t/ℓ^2 as shown in Figure E-1A and E-1B, as well as in Figure E-1C and E-1D. By extrapolating the data to infinite time, M_∞ for the limited volume extraction is estimated at 0.91 M_0 , whereas M_∞ for the "infinite" volume extraction reaches 0.99 M_0 (Figure E-1E).

A comparison of the extraction methods (1) and (2) for poor solvents may be seen from the results for E.5B60 and E.5B60(L) as shown in Figure E-1F. It is evident that the total amount of extraction is much higher in the case of E.5B60 because of large volumes of solvent being used. However, as stated earlier, the kinetic meaning of the data depends on whether an equilibrium partition has been approached before the renewal of the solvent.

Thickness

It was stated previously in the FY78 Annual Report that both the reproducibility (HA60-1, HA60-2) and thickness scaling (HA30, HB30) and (HC24, HD24) by t/ℓ^2 are good. Even though the nature of sample D is somewhat questionable, the results of HC24 and HD24 may be brought much closer together by reducing

the data in terms of t/l^2 . These conclusions may be visualized in a collection of results for the migration of $C_{18}H_{38}$ from LPE into C_7H_{16} as represented in Figure E-2 for M_t/M_0 versus t and in Figure E-3 for M_t/M_0 versus t/l^2 . Therefore, final data involving samples of different thicknesses should be scaled and represented by t/l^2 in order to provide easier comparison.

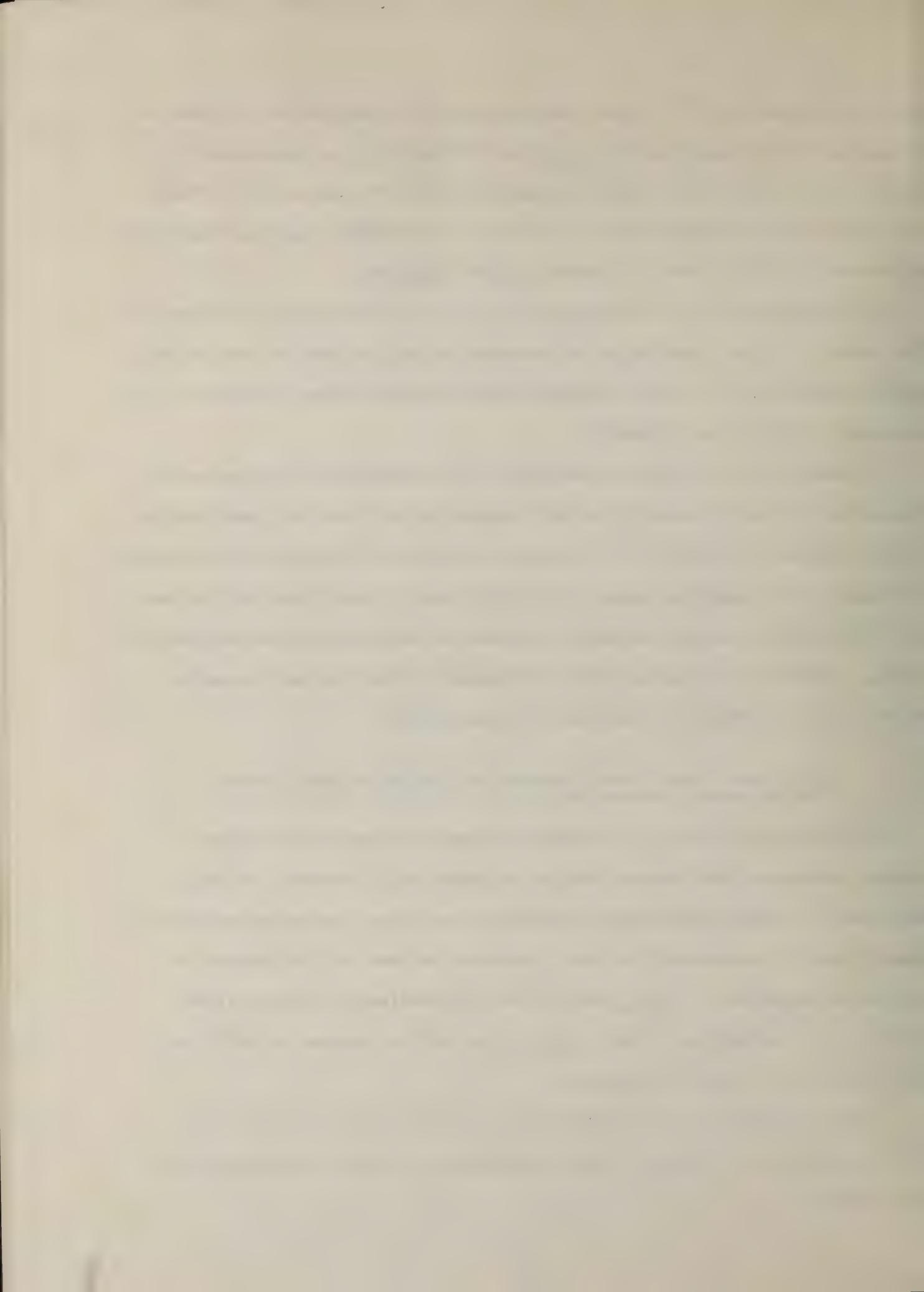
By representing data in the form of M_t/A , or in terms of PPM as defined in CFR, versus t , a good correlation of thickness scaling may also be seen as the initial portions of the curves collapse together as shown later in Figure E-5 for the cases E.5A60L(1) and E.5B60L(1).

It seems that future experimentation may be simplified by eliminating the observation of the thickness effect and considering only the four cases similar to those listed in Tables IV & V. Although the range of thicknesses investigated is limited to the practical range of 0.2 to 0.7 mm, a future check will be made on a thick slab to simulate infinite thickness for migration lasting as long as 6 months. For very thin samples, the total content of the film may be used to decide whether an extraction experiment is even needed.

$C_{18}H_{38}$ into Ethanol/Water Mixtures and Partition Coefficients

At high ethanol content, the migration behavior seems to be Fickian. However, deviation from Fickian behavior increases as the ethanol content is decreased. At 50/50 ethanol/water composition and below, the amount migrated is almost linearly proportional to time. These may be seen in a collection of results for migration of $C_{18}H_{38}$ from LPE into ethanol/water mixtures at 60°C in Fig. E-4. The results of HA60, $C_{18}H_{38}$ from LPE into heptane at 60°C, are also included for comparison purposes.

Below 70% ethanol content, equilibrium partition may be reached due to the low solubility of $C_{18}H_{38}$ at these compositions, as shown approximately in Figure E-4B.



Three experiments (E.5A60L, E.5B60L and E.5C60L) are represented in Figure E-5. For each of the three experiments, new solvents are used to repeat the extraction experiment after a partitioning of $C_{18}H_{38}$ has been reached. The numbers in parentheses denote the successive renewing of the extraction procedures. The similarities in the initial behavior from successive extractions indicate that a redistribution of additive concentration was achieved before the renewal of extracting solvent. The level of initial extraction represented by the mass migrating per unit area is clearly influenced by the overall additive content in the polymer. There is virtually no thickness effect for the initial migration. The final concentration depends on the partition coefficient, the total amount of $C_{18}H_{38}$, and the ratio of the volume of the polymer sample to that of the solvent. The partition coefficient for E.5A60L and E.5B60L, even at different successive extractions, are all at about 0.0012.

The partition coefficient for E.5C60L is, however, about 0.00045. Perhaps at 0.01% additive level, the labeled additive may not represent most of the $C_{18}H_{38}$ present in the polymer. Another possibility is that the dissolution of other oligomers from the polymer may influence the solubility and therefore the observed partition coefficient in 50/50 ethanol/water mixture. As detailed in the FDA Memorandum by Dr. Snyder, linear polyethylene contains about 0.2% of extractable oligomer content having a MW distribution maximum at about 300.

The advantages of the ethanol/water mixtures as simulating solvent for oligomers are that the solubilities may be changed by 5 to 6 orders of magnitudes by changing the compositions (ref. - quarterly report, Oct. 1 - Dec. 31, 1978). However, the same advantageous characteristics are also the cause for concern. During long term testing some evaporation and change of composition may occur. The solubility, and hence the partition coefficient, may be changed drastically during the course of a long extraction experiment. Therefore, the extraction

experiments in volatile mixed solvent systems require rather exacting experimental conditions to avoid the changes in the solvent composition. The type of extraction vials as shown in the last annual report require at least a flat grinding of the vial tops, even better with fine polishing, in order to seal the extraction vials against teflon gaskets.

$C_{18}H_{38}$ into Corn Oil and Trioctanoin

In searching for simulating solvents as substitutes for food oils, the natural tendency is to look for some pure triglycerides to avoid compositional uncertainties. Tributyrin and trioctanoin seem to be readily available. Although tributyrin is much less expensive, trioctanoin is much closer to food oils in the solubilities for $C_{18}H_{38}$. Solubilities of $C_{18}H_{38}$ in various food oils as well as in certain potential simulating solvents will be presented in the future.

At 60°C, the migration behaviors of $C_{18}H_{38}$ into corn oil (CA60L) and trioctanoin (TA60L) are very similar to each other (Fig. E-6). They are also rather similar to that into 90% ethanol (E.9A60L), although in the case of E.9A60L, an eventual equilibrium partitioning may be reached. The migration behavior of $C_{18}H_{38}$ into heptane HA60 is also shown in Fig. E-6 for comparison. It is obvious that, at M_t/M_o about 0.8-0.9, the rate of migration into heptane is about 50 times faster than that in the other three cases. Thus both trioctanoin and 90% ethanol could be considered as simulating solvents for food oils instead of heptane. Their similarities in temperature coefficients and concentration effects may require more thorough comparisons.

The migration behavior for $C_{18}H_{38}$ into trioctanoin is largely Fickian. Some irregularities in the behavior (deviating from a smooth behavior) were observed (Figure E-7). This could be the result of insufficient agitation of the viscous solvent or due to the long term instability of the temperature controller. We have now acquired heating blocks with magnetic stirring devices. The effect of



stirring will be carried out in the near future. A 30°C temperature change from 30 to 60 seems to change the time for extraction by a factor of 30. This is probably related to the large change in temperature coefficient of the viscosity of the solvent.

Migration of $C_{18}H_{38}$ from Branched Polyethylene

We have started migration studies of $C_{18}H_{38}$ from branched polyethylene samples. Preliminary results indicate that the migration rate of HG60 is about 5 times faster than that from linear polyethylene samples HA60 of the same $C_{18}H_{38}$ content and thickness and at the same temperature; otherwise the behaviors are very similar. The diffusion coefficient is about $4 \times 10^{-7} \text{ cm}^2/\text{sec.}$ as compared to 1.6×10^{-7} listed in the table of literature values. In Figure E-8 it is obvious that almost all the added $C_{18}H_{38}$ was removed in about one hour by heptane at 60°C. We will correlate in the future the effects of solvents, and temperature on oligomers in BPE, as well as the effect of crystallinity and with LPE.

Planned Work for the Next Quarter

Tables of apparent maximum diffusion constants corresponding to the five tables of the code scheme are now in preparation and awaiting completion of the experiments. Further work on the migration of $C_{18}H_{38}$ from BPE and experimental work on the migration of $C_{32}H_{66}$ from both BPE and LPE will begin in the next quarter. A plaque of LPE approximately 3 mm thick will be used to demonstrate experimentally the 'infinite' thickness behavior. We will also explore the possibility of using plasma oxidation as a method to determine the concentration profile of the additive and thereby determine the diffusion constant in the absence of solvents.

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Migration of n-C₁₈H₃₈ from Polyethylene
into 90% Ethanol/water Mixture
at 60 °C

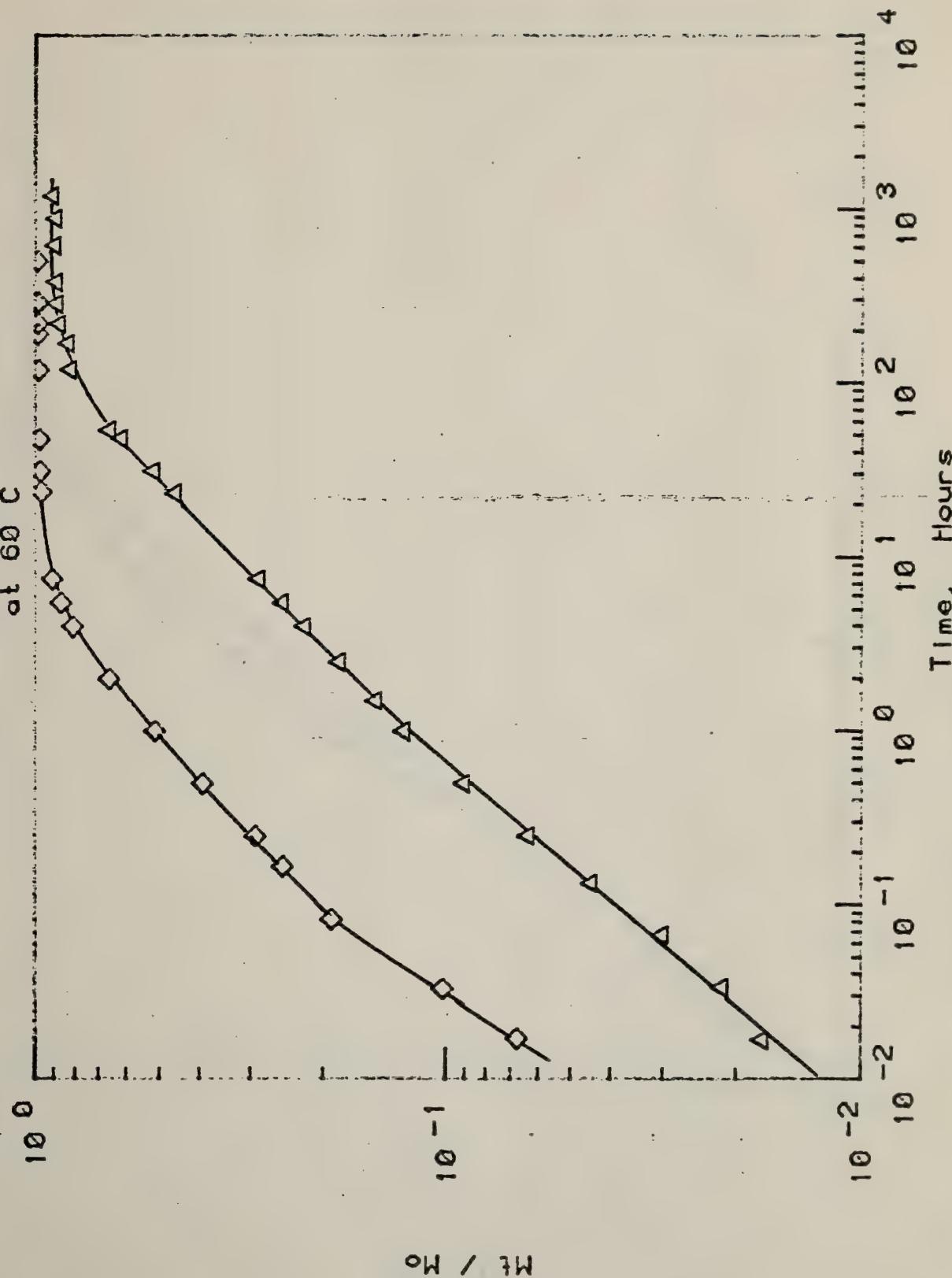


Figure E-1A. Δ E. 9A60I, ◊ E. 9B60

Migration of n-C₁₈H₃₈ from Polyethylene
into 90% Ethanol/water Mixture
at 60 C

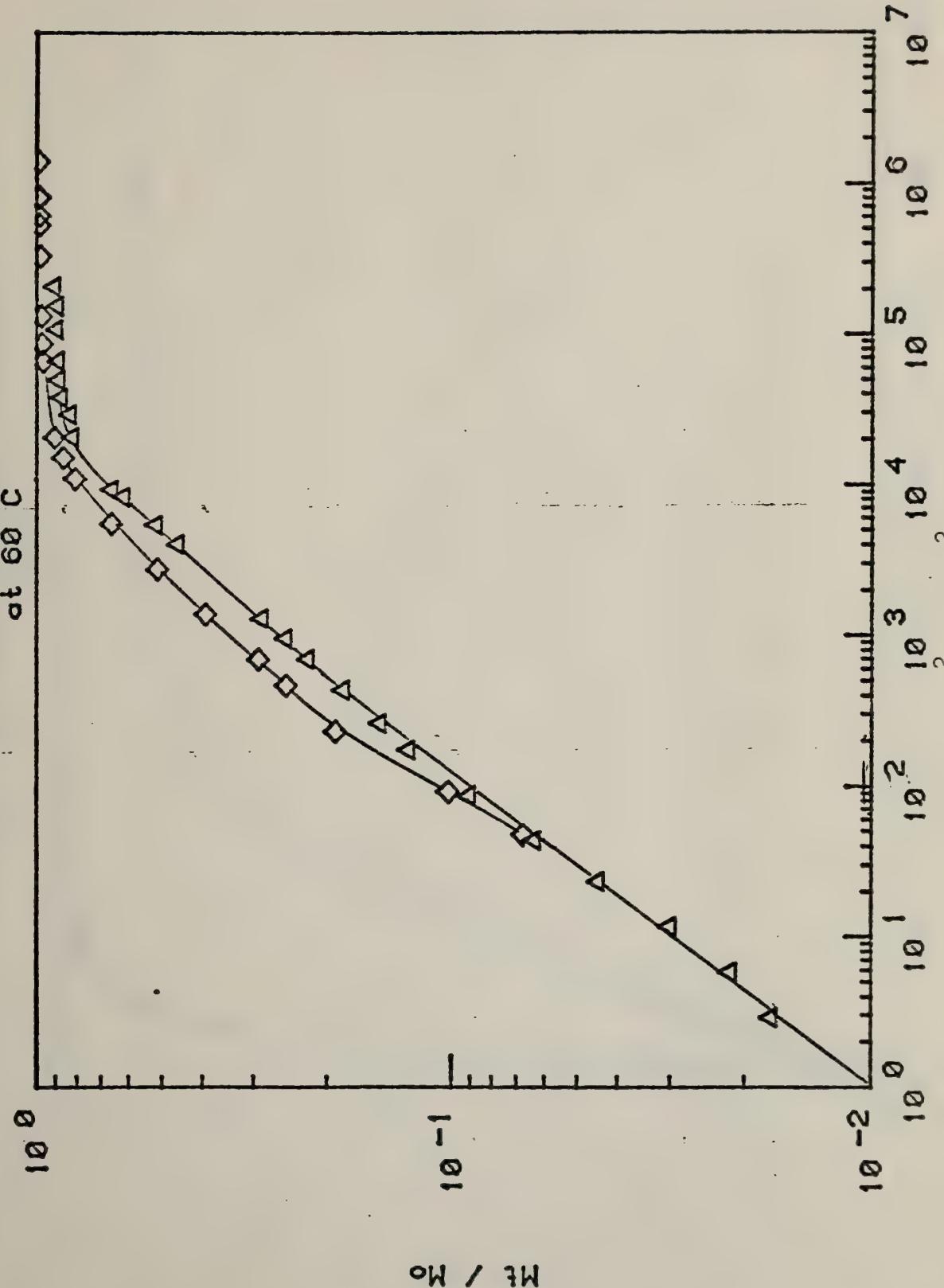


Figure E-1B. Δ E.9A60L, \diamond E.9B60



Migration of n-C₁₈H₃₈ from Polyethylene
into 90% Ethanol/Water Mixture
at 60 C

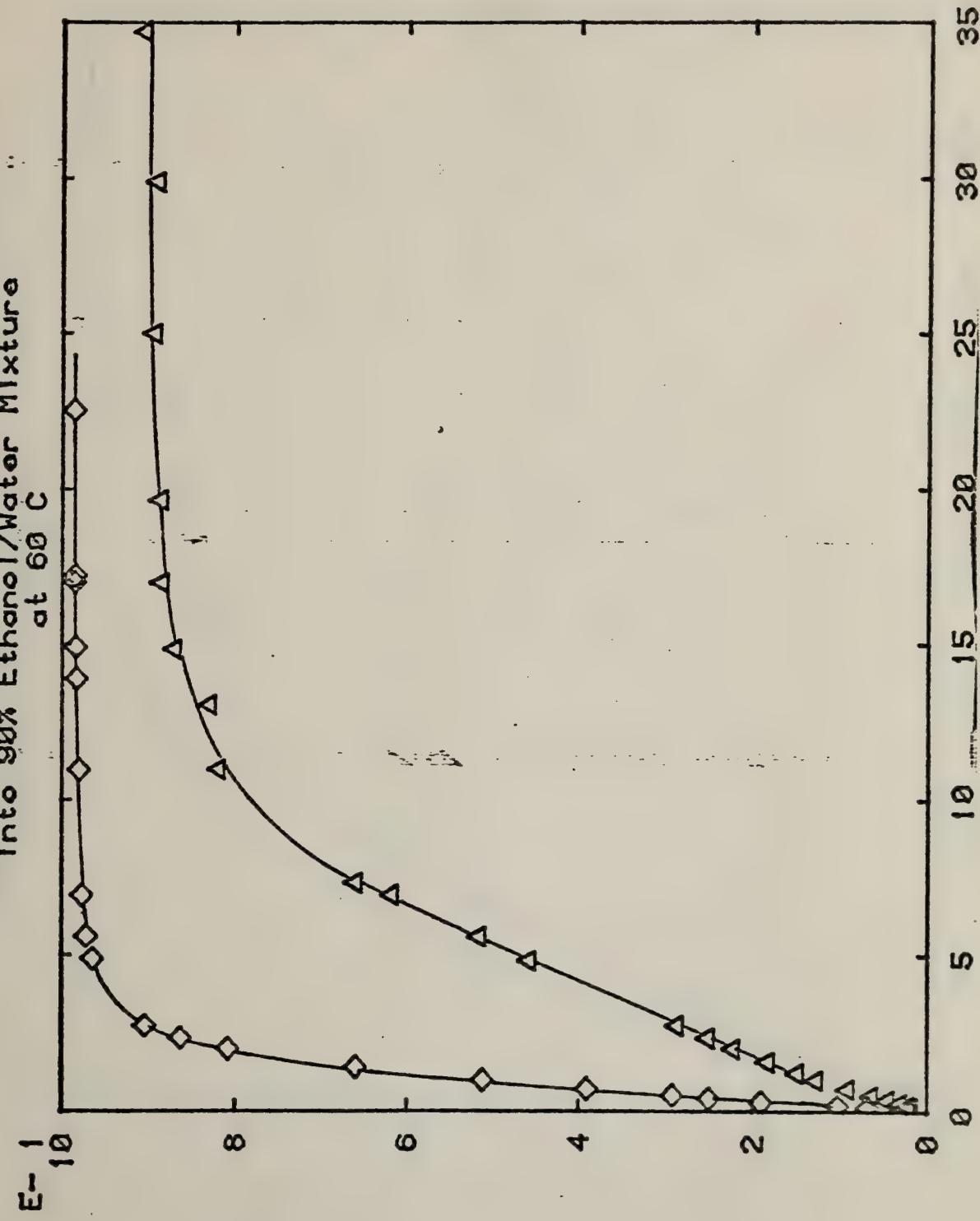
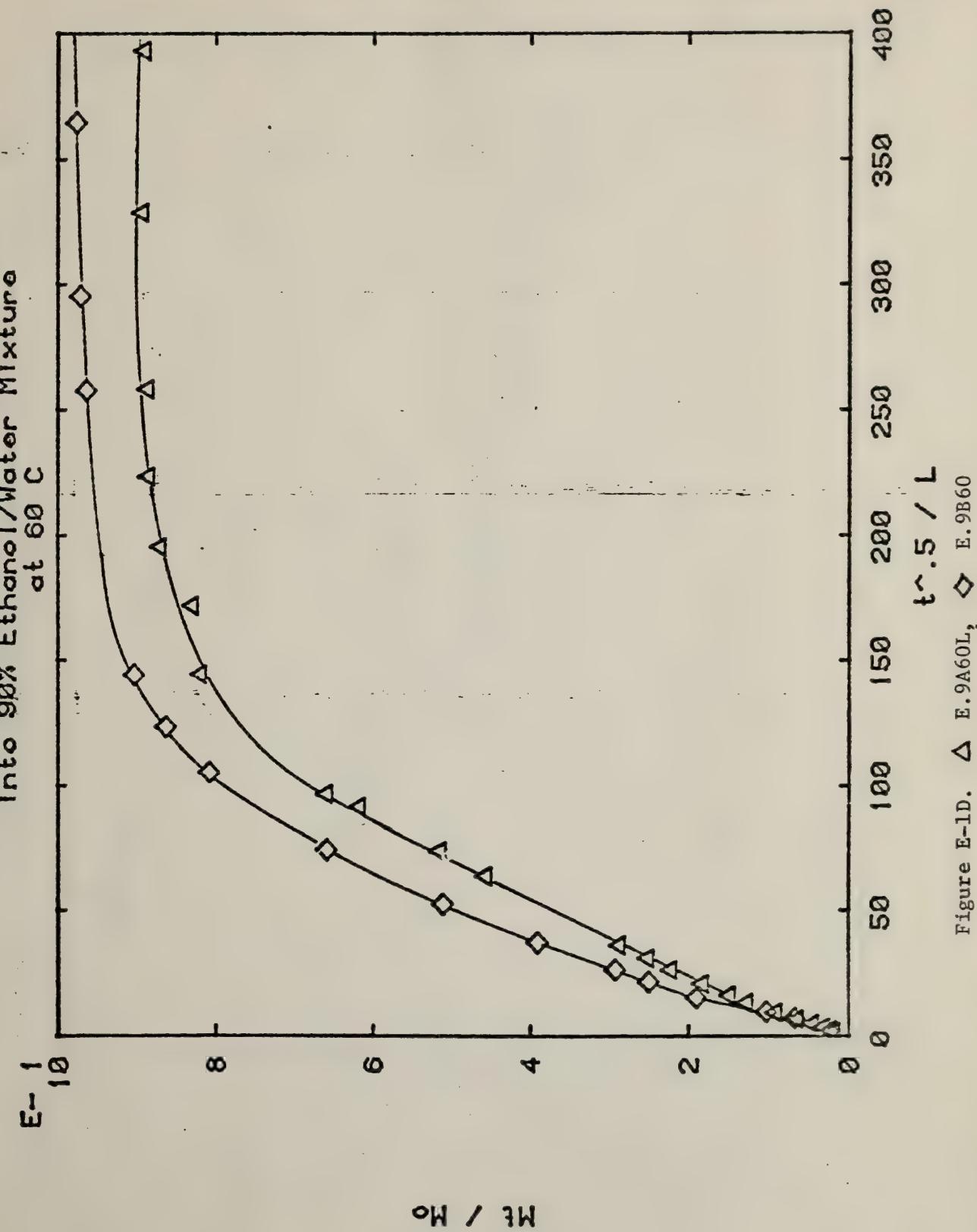


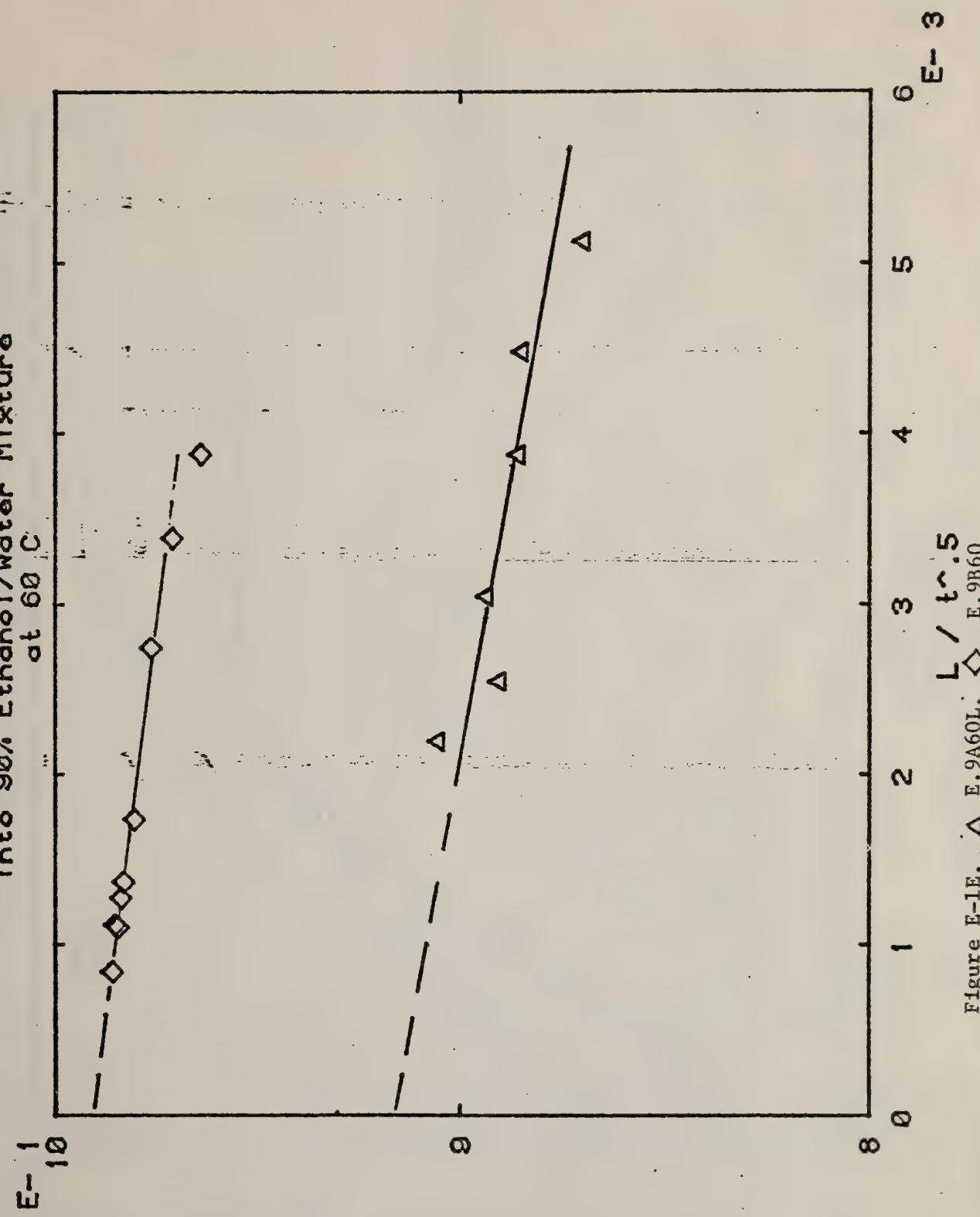
Figure E-1C. Δ E.9A60L, \diamond E.9B60



Migration of n-C₁₈H₃₈ from Polyethylene
Into 90% Ethanol/Water Mixture
at 60 C



Migration of n-C₁₈H₃₈ from Polyethylene
into 90% Ethanol/Water Mixture
at 60°C



O_H / M

Migration of n-C₁₈H₃₈ from Polyethylene
Into 50/50 Ethanol/Water Mixture
at 60 C

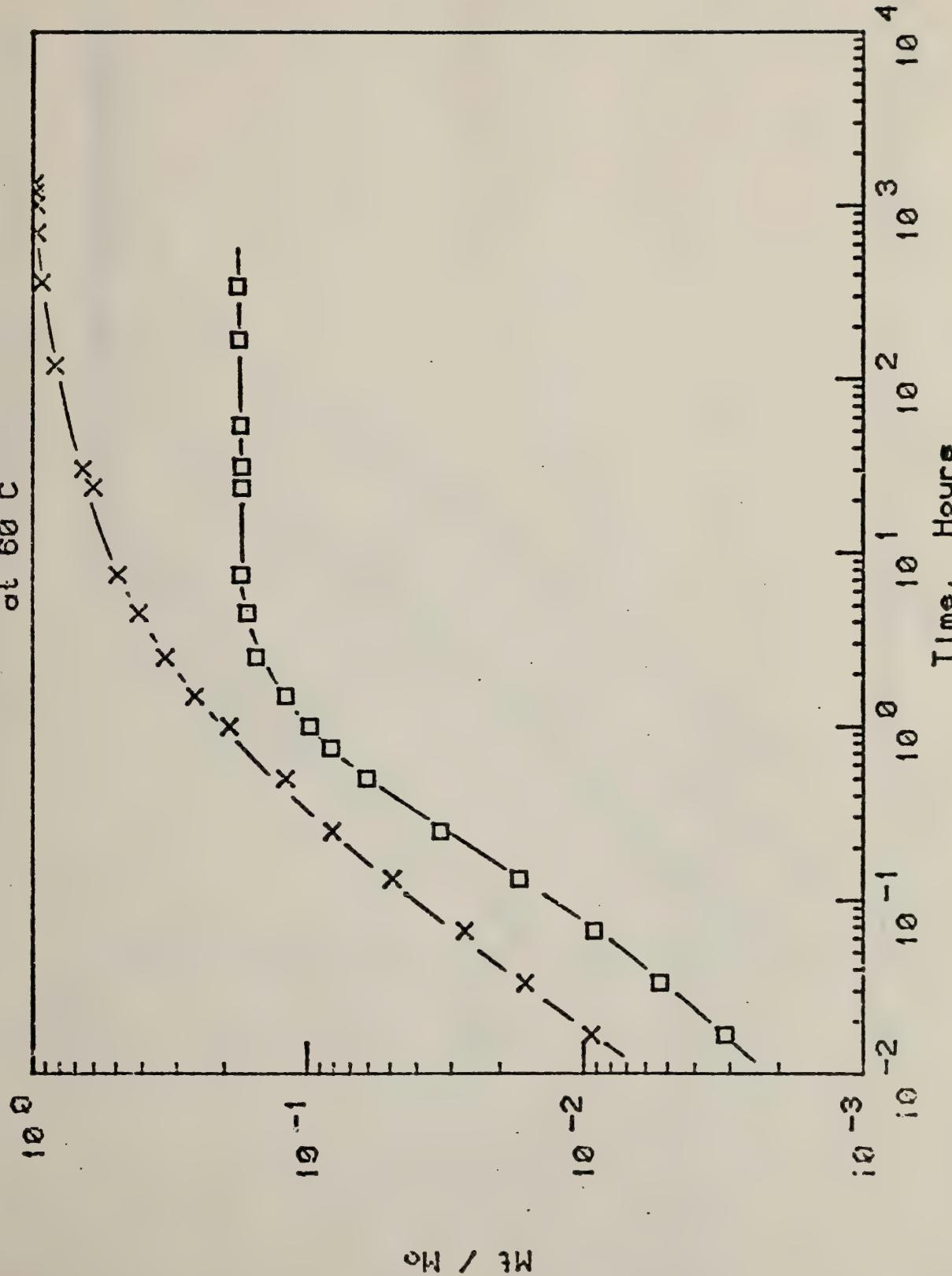
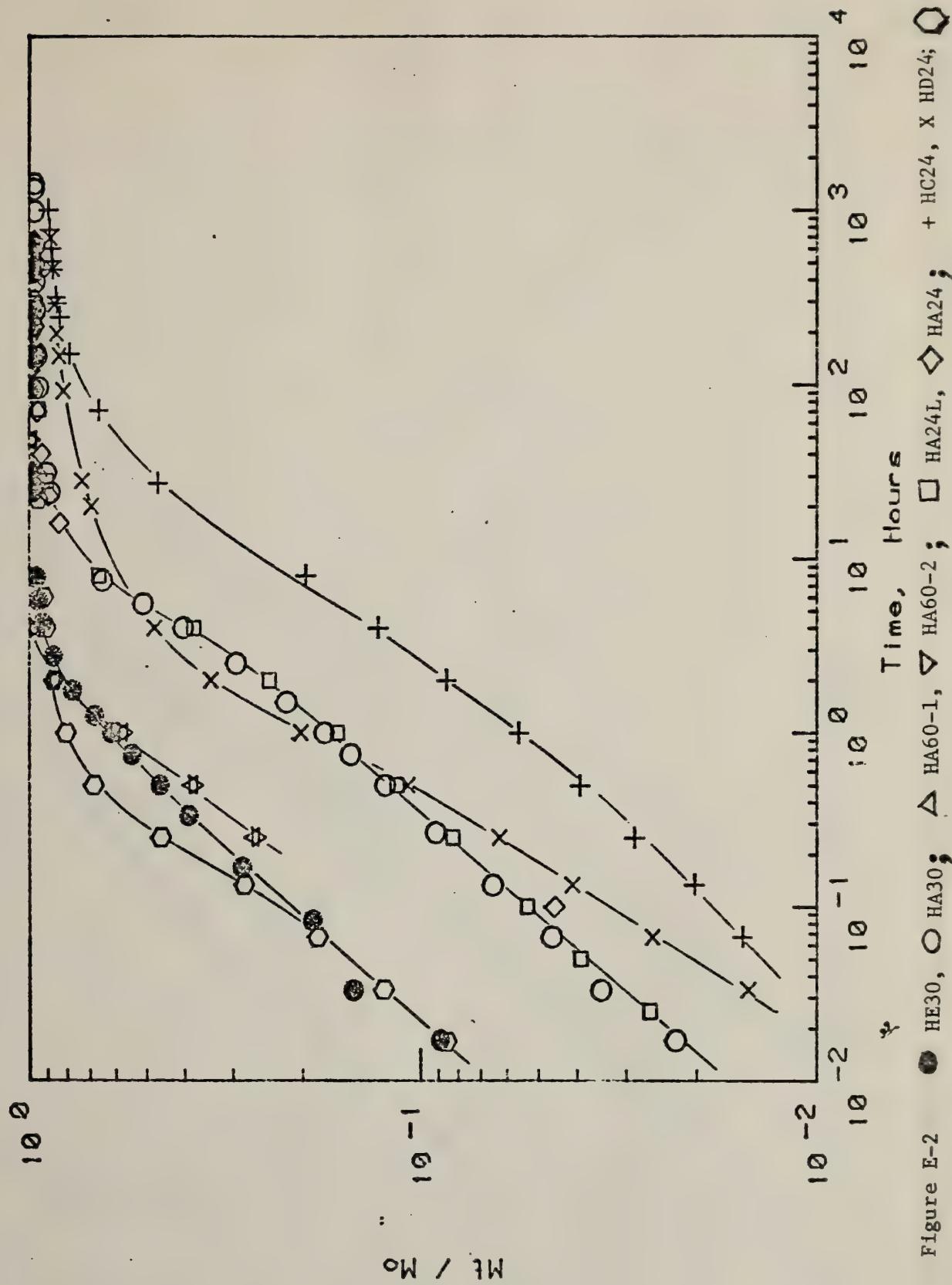


Figure E-1F X E.5B60, □ E.11F

Migration of n-C₁₈H₃₈ from Polyethylene
into C₇H₁₆



Migration of n-C₁₈H₃₈ from Polyethylene
into C₇H₁₆

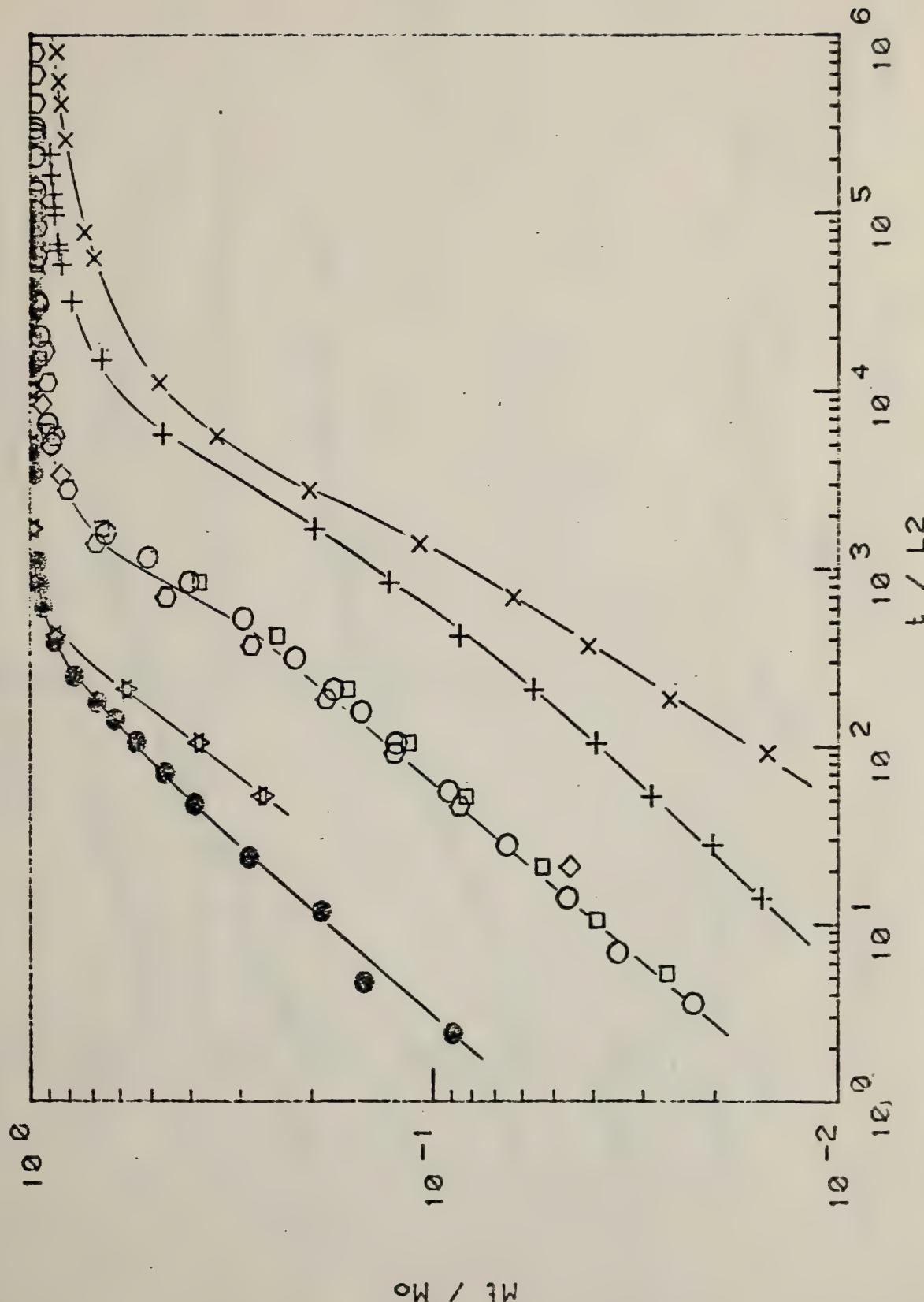


Figure E-3 HE30, \bullet , \circ ; HA30, Δ , ∇ ; HA60-1, ∇ ; HA60-2, \square ; HA24L, \diamond ; HA24, $+$; HC24, $+$; HB24, \bigcirc



Migration of n-C₁₈H₃₈ from Polyethylene
at 60°C

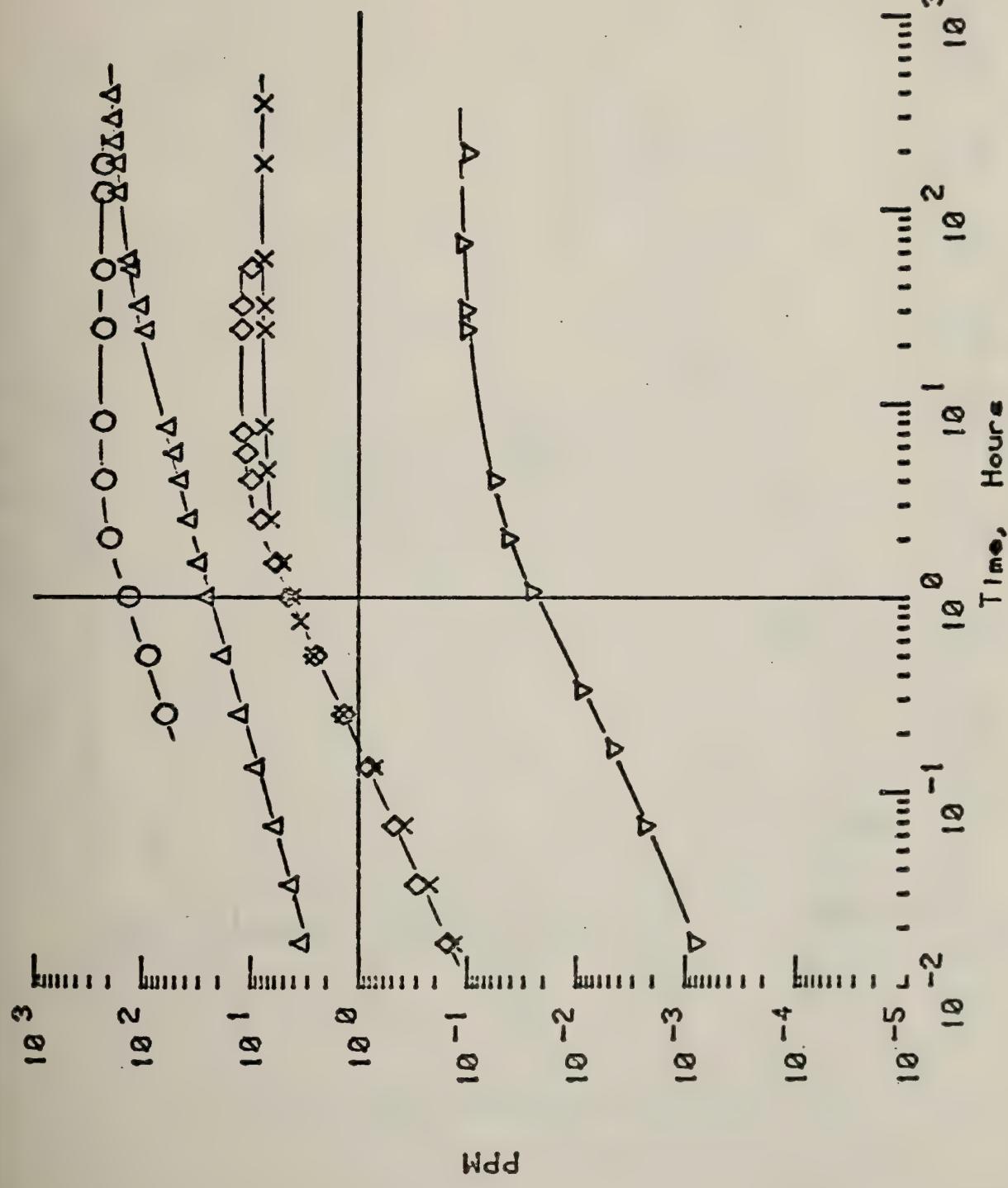


Figure E-4 Δ E.9A60L, \diamond E.5A60L (1), \times E.5B60L (1), ∇ E.5C60L (1), \circ HA60-1



Partition Coefficient of C18H38 between
Ethanol-Water and Linear Polyethylene
at 60°C

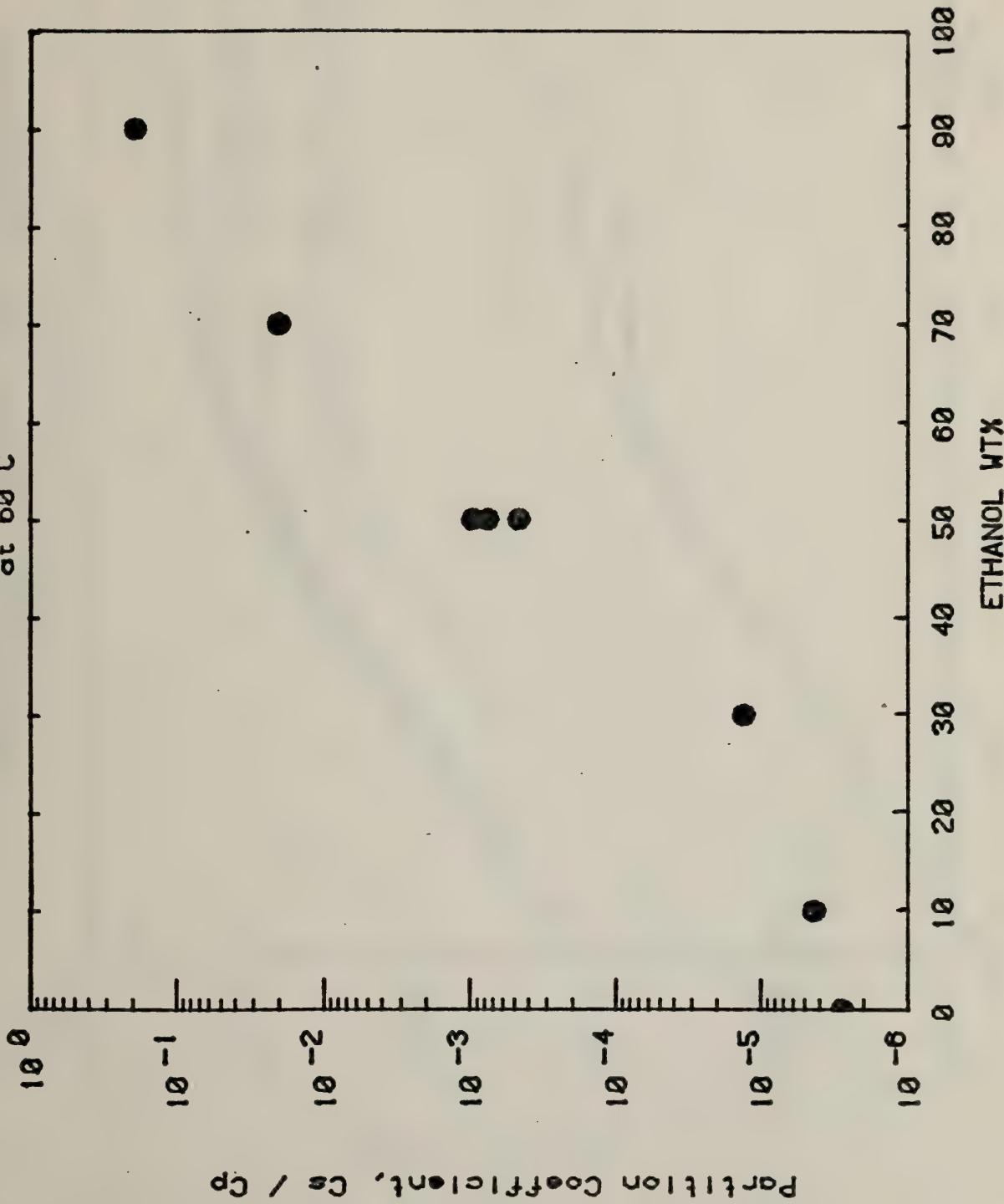
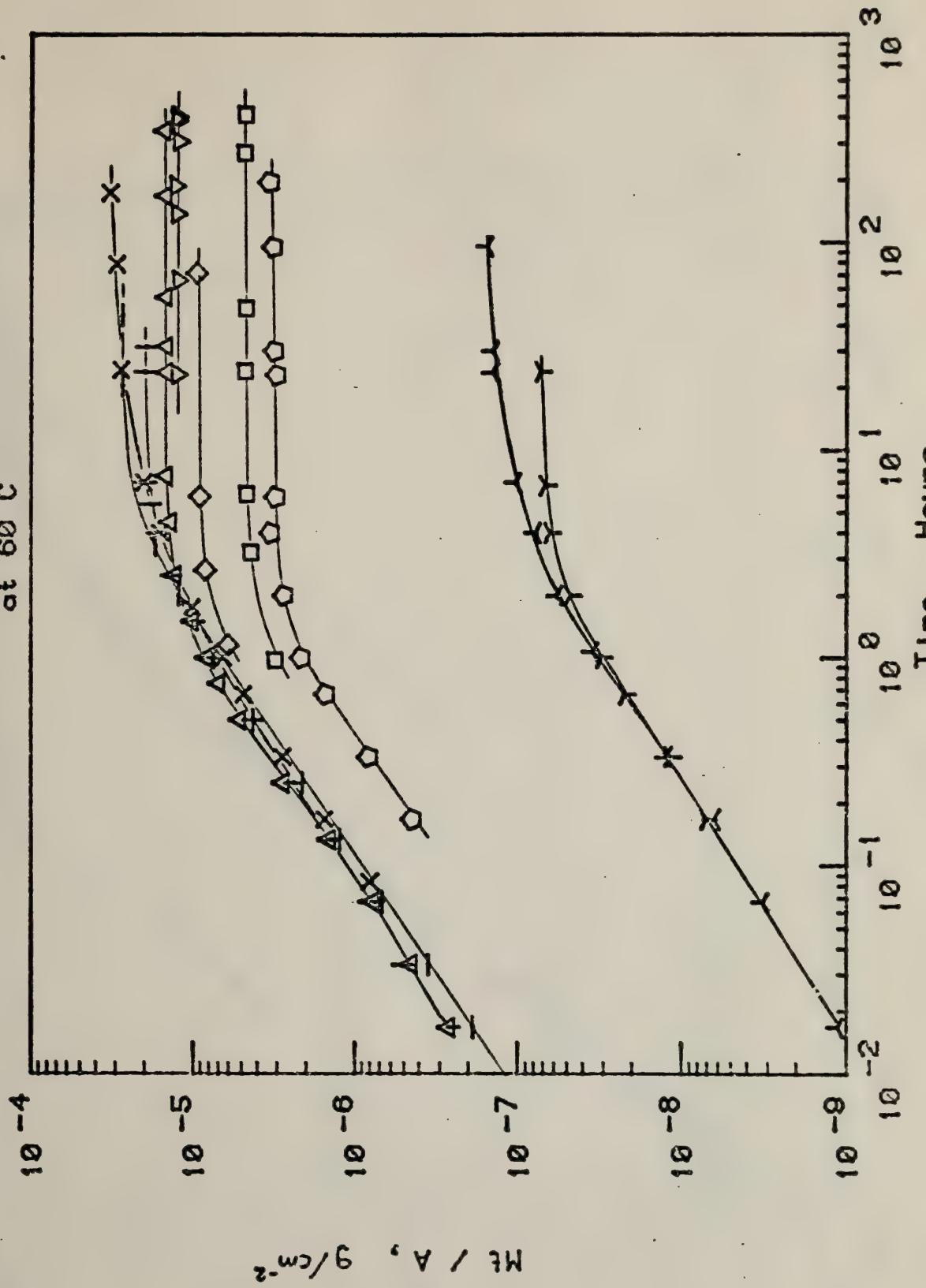
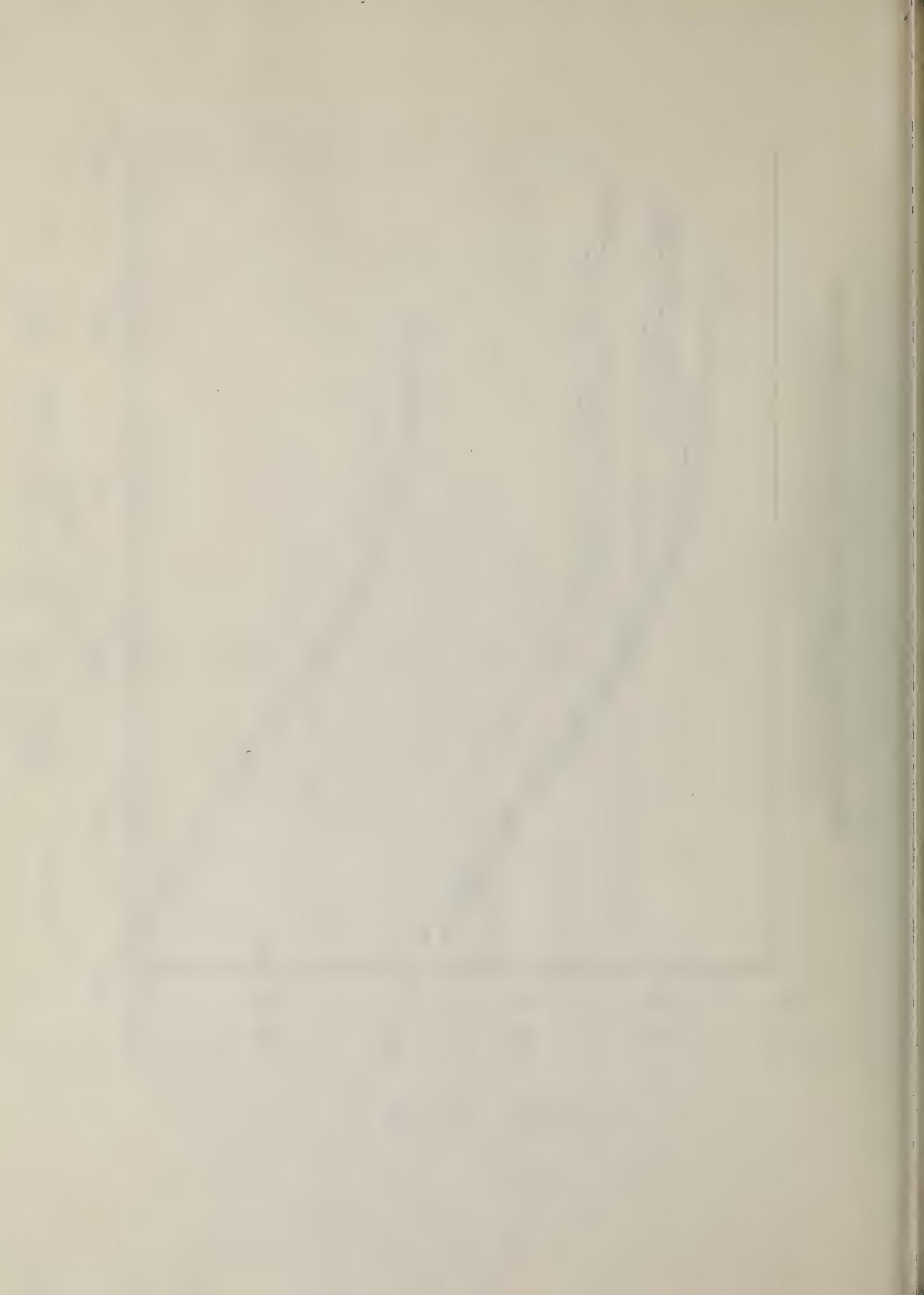


Figure E-4B. Partition Coefficients.

Migration of n-C₁₈H₃₈ from Polyethylene
into 50/50 Ethanol/Water Mixture
at 60 C





Migration of n-C₁₈H₃₈ from Polyethylene
into Corn Oil, 90% Ethanol, Heptane and Trioctanol
at 60 C

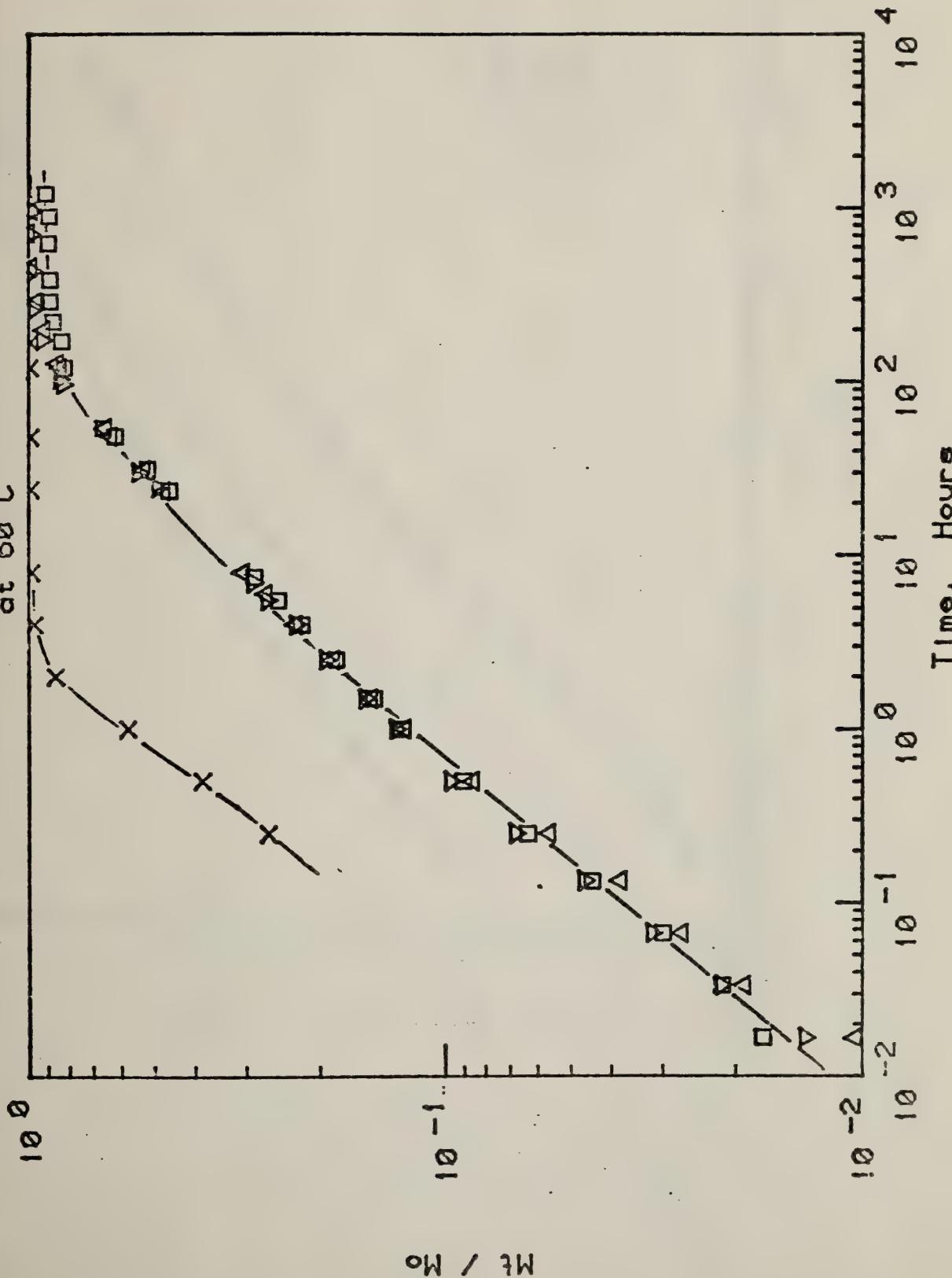


Figure E-6 Δ CA60L, ∇ TA60L, \square E.9A60L, \times HA60-1



Migration of n-C₁₈H₃₈ from Polyethylene
into Triacetin

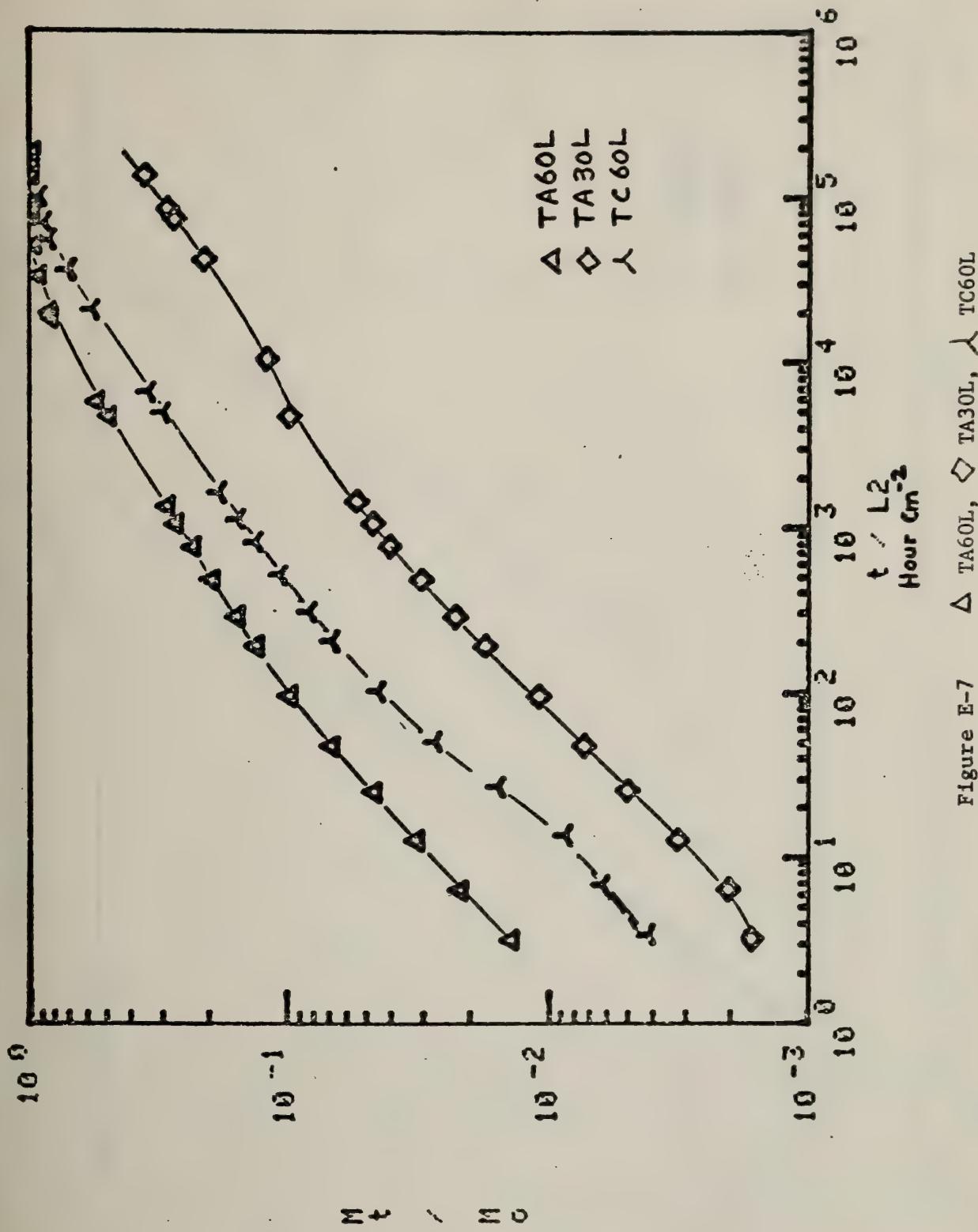


Figure E-7 Δ TA60L, \diamond TA30L, \times TC60L



Migration of n-C₁₈H₃₈ from Polyethylene

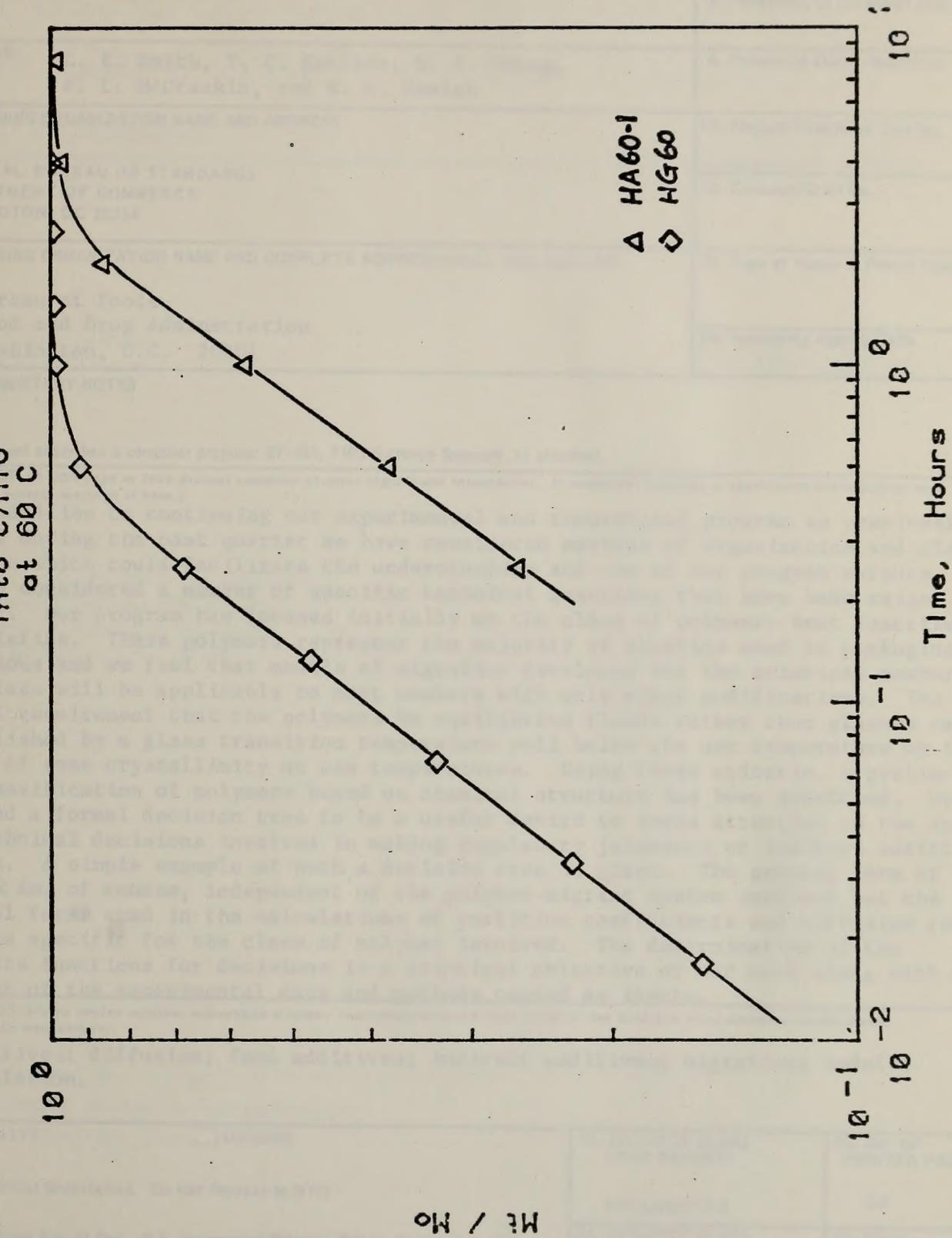


Figure E-8 Δ HA60-1, \diamond HG60

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15. SUPPLEMENTARY NOTES <input type="checkbox"/> Document describes a computer program; SF-185, FIPS Software Summary, is attached.				
16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.) In addition to continuing our experimental and theoretical program as previously described during the past quarter we have considered methods of organization and classification which could facilitate the understanding and use of our program outputs. We have also considered a number of specific technical questions that have been raised by FDA staff. Our program has focused initially on the class of polymers best described as polyolefins. These polymers represent the majority of plastics used in packaging applications and we feel that models of migration developed for the principal members of the class will be applicable to most members with only minor modifications. The technical requirement that the polymers be equilibrium fluids rather than glasses can be established by a glass transition temperature well below the use temperature or by evidence of some crystallinity at use temperatures. Using these criteria, a preliminary classification of polymers based on chemical structure has been developed. We have found a formal decision tree to be a useful device to focus attention on the specific technical decisions involved in making regulatory judgments on indirect additive questions. A simple example of such a decision tree is given. The general form of this tree is, of course, independent of the polymer-migrant system involved but the functional forms used in the calculations of partition coefficients and diffusion constants are specific for the class of polymer involved. The determination of the appropriate functions for decisions is a principal objective of our work along with an assessment of the experimental data and methods needed as inputs.				
17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons) Additives; diffusion; food additives; indirect additives; migration; models; regulation.				
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